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CANDIDATE CHEMICAL SYSTEMS FOR AIR COOLED SOLAR POWERED, ABSORPTION AIR CONDITIONER DESIGN

Part I Organic Absorbent Systems

By
Wendell J. Biermann

Work Performed Under Contract No. EG-77-C-03-1587

Carrier Energy Systems Division
Carrier Corporation
Syracuse, New York

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Solar Energy

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CANDIDATE CHEMICAL SYSTEMS FOR AIR COOLED, SOLAR POWERED, ABSORPTION AIR CONDITIONER DESIGN

PART I - ORGANIC ABSORBENT SYSTEMS

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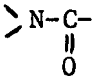
Dr. George Rusin, Senior Chemical Engineer
Mr. Richard Kyanka, Chemical Technician

ABSTRACT

All the available experimental evidence suggests that the optimum "organic" absorbent/refrigerant combination would be a methane derivative with a single hydrogen atom with chlorine and fluorine atoms in the other sites, as refrigerant. This would be hydrogen bonded to an absorbent molecule containing the group  $>N-\overset{\overset{\displaystyle O}{\|}}{C}-$, with the substituent groups being such that no steric hindrance took place.

Cycle analyses showed that the ratio of internal heat transfer to cooling would be large, probably impractically so in view of the high coefficient of performance needed for solar driven cooling and the additional handicap of heat rejection to the atmosphere.

A more promising approach would be to reduce the internal heat transfer per unit of space cooling by selecting a refrigerant with a high latent heat of vaporization and selecting an absorbent with suitable properties.

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1-0 INTRODUCTION

There has been a lengthy study, extending back into the nineteenth century, identifying various chemical combinations which can support economically acceptable absorption cooling cycles for space conditioning. Of the many cycles which have been studied, only two have been developed to real commercial status. These two systems are ammonia-water, which first appeared as a gas powered, household refrigerator (by Servel) and later as a small tonnage space conditioning device (by Bryant, Arkla and Whirlpool) and the lithium bromide-water cycle which was a profitable product in the hundred ton and larger size (Carrier, Trane and York) but which struggled without notable success in the smaller sizes (Servel and others).

Both of these systems have limitations which have restricted their areas of application and have periodically led to renewed efforts in the search for alternate chemical combinations. Some of the more important limitations to these two cycles are:

1-1.1 <u>Aqua-Ammonia</u>

Ammonia is a toxic, flammable refrigerant, hence cannot be used for direct expansion in an occupied space. Because it is a high pressure system, the generator is covered by code requirements which, for the direct fired version, effectively limited the generator diameter to six inches and restricted the equipment to small tonnage modules. The high pressure of the generator-condenser portion also presented a pump problem in both mechanical design and as a parasitical load. Various "trap" systems in which high pressure vapor was used to supply the necessary head have also been used, but for a variety of reasons were displaced by pumps. In an effort to raise the coefficient of performance of the unit, a high generator temperature was used (about 190°C solution) and a large amount of heat transfer surface which led to high costs and large equipment size.

For solar application, a serious limit is encountered in that decreasing the generator solution temperature to temperature regimes accessible to contemporary solar collectors, fluids and storage art, causes a decrease in the concentration difference between strong and weak streams, hence an increase in the pumping rate required to maintain capacity. This causes an increase in the pump power to the point that when the currently accessible solar collector temperature regime is approached, the pump energy requirements have become greater than the power needed to drive a compression cycle of similar capacity. An increase in solution circulation rate also requires that heat transfer surface increase to avoid deterioration in net thermal efficiency.

At a time when promotion of natural gas for summer consumption was a major business thrust for the gas utility industry, the manufacture and sale of aqua-ammonia chillers was economically possible. Now that natural gas has ceased to be an abundant and very low priced energy source, the aqua ammonia chiller is on the verge of vanishing from commerce.

1-1.2 Lithium-Bromide-Water

This cycle has traditionally been used with low temperature steam at about 115°C, which is in a range marginally accessible to solar collectors of the present period. With suitable modifications these units can be adapted to lower temperature easily available from evacuated tubular, moderately concentrating or even good, flat plate collectors. One problem exists, however; the lithium bromide-water cycle has not been practically developed in a manner which can be air cooled. The lithium bromide-water system has been (commercially) liquid cooled, with a cooling liquid source which cannot rise much above 30°C, an inherent limitation based on the finite solubility of lithium bromide in water.

For large installations, it is economically acceptable to supply a stream of recirculated water whose temperature is within the acceptable temperature limits by evaporative cooling, most conveniently with a cooling tower. A great deal of the failure of smaller lithium bromide units to win significant market acceptability has been charged to the unwillingness of householders, storekeepers and other users of low tonnage air conditioners to accept the additional first cost and maintenance of evaporatively cooled absorption equipment.

The most fertile period for the study of absorption refrigeration combinations was the decade of the 1930's when many pairs were investigated; unfortunately, however, most of the investigations were too superficial to draw any real conclusions. From this early work the two systems commercialized emerged and further exploration for new systems remained at a low level until the gas utility industry began to sponsor programs seeking the development of direct gas-fired space conditioning equipment. Most of this work lay dormant during the period between the time when the emergent energy shortage intruded itself into the public consciousness and the resurgence of interest in heat operated cooling devices caused by Federal financing of solar and geothermal programs.

1-1.3 Objectives of This Project

The first task of the present project, ERDA Letter Contract No. EG-77-C-03-1587, is to present a status report of the various systems which might be capable of sustaining the development of a product line of air cooled absorption units of "residential" size which will be interpreted as the capability of supplying 10,000 watts of cooling. The conditions under which this rating will be measured will specify water (or other acceptable fluid) being supplied to a cooling coil in an air stream at 7°C and the water returned to the chilling device at 13°C. Heat will be rejected, when rating, to an air stream at 35°C and incoming energy will be in a fluid at 110°C.

In addition to arriving at certain recommended areas for additional development work, these reports will also serve as resource documents wherein data supporting our conclusions can be recorded and made available to other investigators who may wish to draw different conclusions. At the very least, it may save repetition of experimental work which has already been done several times by industrial groups pursuing parallel programs.

Anticipating what will develop in subsequent sections, postulating a heat source at 110°C is a very serious restriction, in that the concentration difference between strong and weak solutions becomes small (particularly if approach temperatures within the limits of practicality are also accepted). The consequences of small concentration difference are increasing need of heat transfer surface, decreasing coefficients of (thermal) performance and rising electrical requirements for pump power.

In spite of the severe limits the 110°C energy source imposes, the writer feels that it must be accepted for the present since this appears to be a reasonable assessment of the performance which current solar technology can supply with "reasonable" solar conversion efficiency.

It is planned to issue this report in three sections classified by nature of absorbent:

1. Organic liquid absorbents
2. Soluble solid absorbents
3. Salt - "antifreeze additive" absorbents.

2-0 ORGANIZATION OF SEARCH

In principle, any two substances with different vapor pressure-temperature relationships and some degree of miscibility can be used for absorption cooling. To be practical, however, there must be a definable difference between the temperature levels of the energy intake (chiller) and the energy discharge (absorber and condenser), which is equivalent to saying that the vapor pressure of refrigerant dissolved in the absorbent at whatever temperature it is practical to cool it, must be lower than the vapor pressure of pure refrigerant at the temperature needed to cool the space concerned. In the case of water cooled absorption equipment, this difference between evaporator and absorber temperature is about 25 to 30°C; for an air cooled system it will be in the vicinity of 40°C. A second requirement is that this depression of the vapor pressure of the refrigerant when dissolved in the absorbent be experienced with the refrigerant being a significant portion of the solution since this is one of the factors which affects overall cycle efficiency. Traditionally, these requirements are summarized in the requirement that a marked negative deviation from Raoult's Law will characterize a candidate absorbent-refrigerant combination. This is a useful statement because it permits considerable screening of the nearly limitless number of conceptually possible absorbent-refrigerant pairs. Unless the two chemical species proposed are capable of reversible chemical interaction, negative deviations from Raoult's Law cannot take place.

2-1 SCREENING OF REFRIGERANT CANDIDATE

When establishing criteria of those candidate systems which will be treated experimentally, it is most practical to begin with refrigerants. A few requirements and some highly desirable properties permit rapid reduction to a manageable number of candidates. These will comprise the following:

Chemical Stability. This is a fairly broad term since irreversible chemical reactions with the atmosphere, with the materials of construction of the absorption machine, with the absorbent or simple thermal decomposition must be virtually absent.

Safety Considerations. It is important that the refrigerant not be notably toxic or otherwise dangerous to human beings exposed to liquid or moderate concentrations of vapor. It is highly desirable that the refrigerant not be flammable since flammable refrigerants must be handled in accordance with codes which are reflected as thermodynamic and cost handicaps.

Molecular Weight. The specific heat of vaporization is roughly in inverse proportion to molecular weight whereas specific heat capacity is approximately independent of molecular weight. The ratio of specific heat capacity to specific heat of vaporization is one of the principal quantities affecting the amount of heat which must be handled by internal heat transfer per unit of cooling delivered to the load.

A second consideration of molecular weight is boiling point, which for homologous chemical series tends to increase with molecular weight. A high boiling point refrigerant will have a low pressure in the evaporator-absorber sections and require inconveniently large vapor passages to keep capacity up and simultaneously would complicate any liquid-gas heat exchange which might be desirable to improve the coefficient of performance.

Substances with very low boiling points present problems in designing to safely contain the high pressures of the generator-condenser section and even more troublesome are the mechanical design and power consumption of the pumps.

An ideal refrigerant would boil just below the evaporator temperature so as to maintain a positive pressure inside all portions of the machine; boiling points of -45°C and +110°C are reasonable limits to set for a search.

Functional Groups

Chemical interaction between molecules is not generalized but concentrated in molecular orbitals associated with "functional groups." For interaction between organic molecules, at least for our present purposes, one looks for pairing of molecules, one of which carries a functional group which has an available orbital relatively deficient in electron density (Lewis acid) and the second of which has an orbital with high electron density (Lewis base). Overlapping of these orbitals is then the source of a minimum in potential energy which we associate with an interaction causing a negative deviation from Raoult's Law.

We have found that those refrigerant species which meet our other requirements are generally Lewis acids. It was anticipated that olefins with strongly electronegative substituent groups, such as halogens, would comprise the most useful class of refrigerants for this investigation. As results were accumulated, however, it soon became apparent that the bonding mode was invariably a hydrogen bond between a strongly (Lewis) basic site on the absorbent molecule and a hydrogen site on the refrigerant, with substituent groups on the refrigerant·enhancing the (Lewis) acidity of the hydrogen site.

Section 2-3 contains an account of spectroscopic studies which were carried out to confirm this conclusion.

Other Considerations

A practical refrigerant must have availability at a reasonable cost, must not involve any restrictions (such as high viscosities) to heat transfer and circulation and must not have any inherent slow steps in mass transfer in whatever absorption process is used (resulting in failure to approximate equilibrium conditions).

2-1.1 Candidate Refrigerants

Available refrigerant classes, in terms of our above criteria, comprise:

1. Highly, but not completely, halogenated methane, ethane and ethylene compounds. Samples of virtually all possible members of this group were obtained and tested with "best" absorbent candidates.

2. A few low molecular weight alcohols, ketones and esters are conceptually useful and some of these will be discussed in subsequent reports.

3. Ammonia and lower molecular weight ammonia derivatives possess many of the desirable properties listed above but it will be most convenient to consider the organic absorbents used in a later report along with competitive inorganic systems.

4. Several materials, somewhat unique in their properties, have been considered, among which would be water, hydrogen fluoride, some of the volatile boron hydrides and halides, hydrogen sulfide, carbon dioxide, sulfur dioxide, oxides of nitrogen and other more or less esoteric compounds of the non-metallic elements of the upper right hand section of the periodic table.

   With the exception of water, which is a uniquely desirable refrigerant in many respects, these other elements and compounds can be generally eliminated by their known chemical and physical properties.

2-2 ABSORBENT CANDIDATES

When the basic postulate, that the refrigerant candidates will be electron accepting Lewis acids, is made then the absorbent search narrows down rapidly to a manageable number of materials since the factors relating to the basicity needed in the absorbent are well known.

The more important considerations for selecting absorbent candidates would include the following:

Basic Functional Group. The most strongly electron denoting functional groups are found among the disubstituted amides. This fact was recognized by previous workers, notably by G. F. Zellhoefer, M. J. Copley and C. S. Marvel(1)(3)(4), by C. S. Marvel, M. J. Copley and Emanuel Ginsberg(2), and by Thieme and Albright(5) who recognized the value of the N,N dimethylamide grouping in forming hydrogen bands to partially fluorinated and chlorinated hydrocarbon molecules.

This observation was not followed up by Zellhoefer's group but in this report the most promising organic absorbent systems are based on substituted amine groups.

High Boiling Point. An absorbent should have a considerably higher boiling point ($\Delta T > 100°C$) than the refrigerant to obviate the need for rectification, which involves both machine cost and energy loss. In Zellhoefer's early work, he chose as an absorbent the dimethyl ether of tetraethylene glycol over the amides, whose superiority he recognized, primarily because those amides available to him had low boiling points.

As boiling points rise, melting points generally tend to rise also. A solid absorbent, provided it has very high solubility in the refrigerant, is acceptable but opens one to the risk of solidification of portions of the chiller. We have tried to work with low melting (M.P. < 20°C) materials as much as possible to eliminate the need for design and controls to protect against solidification.

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(1) J. Am. Chem. Soc. 60, 1337-1343 (1938).

(2) loc. cit. 62, 3109-3112 (1940).

(3) U.S. Patent 2,308,665 (January 19, 1943).

(4) U.S. Patent 2,149,948 (March 7, 1939)

(5) 68th Annual ASHRAE Meeting (1961).

Chemical Properties. Given an absorbent with suitable function group and boiling point for the refrigerant, other chemical properties parallel those important for the refrigerant. Low molecular weight is generally desirable because only the functional group is important in absorbing refrigerant. The remainder of the molecule usually does nothing except lower the vapor pressure and contribute to energy losses by its contribution to sensible heat in heat exchangers, flashing, etc. As will be noted below, we have been able to build up a high "concentration" of function groups by placing two such groups on very short hydrocarbon skeletons without sacrificing vapor pressures.

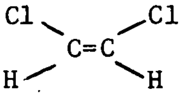
Thermal stability of candidate systems, including absorbent, refrigerant, all materials of construction, should be demonstrated before proceeding too far in qualification. When designing for ten or twenty-year life expectancy, chemical reaction rates must be almost immeasurably slow.

2-3 SPECTROSCOPIC STUDIES OF ABSORBENT-REFRIGERANT INTERACTION

Infrared spectrographic analysis was used to determine the mechanisms of association between various absorbent and refrigerant molecules. The establishment of these mechanisms is an important step when studying the broad field of absorption refrigeration, in order that predictions can be made for "improving" refrigeration combinations.

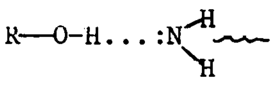
Initial speculation led us to believe that the effectiveness (vapor pressure lowering, etc.) of combining certain olefins (refrigerant) with formamides such as N,N-dimethyl hexamide (absorbent) was primarily due to π-bonding between the carbonyl of the formamide and the π-electrons of the olefin. It was proposed that an electron deficiency resulted at the double bond of olefins containing electron withdrawing groups, such as chlorine, attached to the double bonds. These unfilled π-orbitals overlap with the electron cloud of the unshared electrons of the carbonyl oxygen from the formamide to form the molecular association.

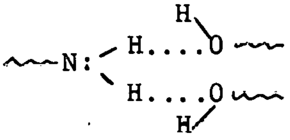
Since the infrared spectroscopic bands of the compounds studied were well characterized in the literature, we could test our premise. One would expect spectral shifts primarily in the carbonyl of the formamide and the C = C bond of the olefin. Other minor shifts in the C-H and in the C-X bands of the olefin might also be expected. The results, however, showed that the largest spectral shift was in the C-H stretching band of the olefin. The second largest was the = C-H bending mode with very minor shifts in the C = C and C-Cl (when chlorinated olefins were used) bands. No apparent change was noted in any bands of the formamide.

From this evidence a completely different mechanism was postulated. The primary association is now believed to be hydrogen bonding between the carbonyl oxygen and the olefinic hydrogens. With compounds where substantial vapor pressure lowering was noted, i.e., cis - 1, 2-dichloroethylene , the carbons to which the electronegative groups were attached, invariably also contained hydrogen. The electronegative group is believed to withdraw electron density from the C-H bond thereby making the proton readily available for hydrogen bonding with the negative C=O group of the formamide. This conforms well with the experimental results since the major spectral shift to be expected would be in the C-H band with only minor secondary perturbations of the C=C and C-Cl bands. Very little change would be expected in the C=O band of the formamide for several reasons: 1) The C=O bond is much stronger (rigid) than the C-H bond of the olefin, therefore would be much less perturbed by electronic interaction; 2) Similarly the mass of the proton is small relative to the oxygen and is more easily polarized; and 3) The strength of the hydrogen bond formed is relatively weak.

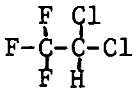
From the experimental results obtained with some of the halogenated olefins such as 1,1-dichloroethylene, 1,2-dibromoethylene, and trichloroethylene, one can correlate vapor pressure lowering effects with the availability and number of active hydrogens. This is essentially corroborated with the infrared results which always showed the major spectral shifts to be in the C-H band. In one case where weak association was expected (trichloroethylene) from vapor pressure data, a larger shift than expected was found. Only one hydrogen is present in this molecule rather than two, therefore the quantitative correlation was rationalized. One can successfully correlate the entire list of olefins tried using proton availability and number, with steric considerations necessary in a few instances.

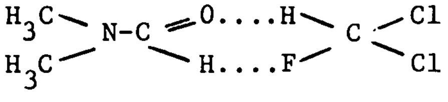
Another interesting group of refrigeration combinations studied was the amine with hydroxynitrile and its analogues. Again, infrared analysis revealed that the interactions are primarily due to hydrogen bonding. Large spectral shifts are seen in the OH bands (200-300 cm^{-1}) of the absorbent molecule and also in the NH_2 region of the amine. Although a literature search revealed hydrogen bonding to nitriles of the type $- C \equiv N...H -$, this is believed to be a minor effect as compared to the bonding to the OH. This conforms with the vapor pressure lowering results which show large pressure lowerings of amine only when the absorbent molecule contains an OH group. The possibility of an inductive effect being exerted on the OH by the $C \equiv N$ group has not been ruled out. Also complicating this system is the possibility of a competition existing between inter and intramolecular hydrogen bonding since the hydroxynitriles have been shown by us to hydrogen bond to themselves. The types of hydrogen bonding one expects in this system are (ignoring the nitrile end of molecule):

1) 

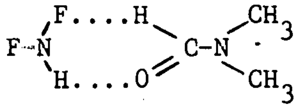
2) 

or combinations of 1) and 2). The type of hydrogen bonding involved remains to be determined, and its verification should aid in predicting better molecular combinations for this system.

Using the hypothesis that hydrogen bonding was the primary source of association between absorbent and refrigerant molecule, we attempted to increase the strength of association by improving the proton donor ability of substituted methanes and ethanes. This was accomplished by substituting fluorine on the carbon containing the proton to give compounds such as R21 ($CFCl_2H$), R22 (CF_2ClH), or  $F\text{-}\overset{F}{\underset{F}{C}}\text{-}\overset{Cl}{\underset{H}{C}}\text{-}Cl$, which are commercially available. All of these type compounds, when combined with formamides, gave much improved vapor pressure lowerings over any chlorinated olefins or saturated hydrocarbons. The improved electron withdrawing capability of the fluorine weakens the C-H bond, consequently making the proton more available for hydrogen bonding. Besides the strong association of this type of refrigerant with formamide absorbents, low molecular weight, inertness, etc. of refrigerant make this combination look most promising. Stronger association can no doubt be found, although reversibility becomes an increasing problem.

As an added reason for the strong association in this system, the possibility of hydrogen bonding to the fluorine must also be considered. With dimethylformamide (DMF) and, for example, R21, one could hypothesize bonding of the type  as a reason for the greatly improved vapor pressure lowering.

Although thermal stability will probably be the major limiting factor when choosing the best absorption refrigeration combination, the trend seems to be clearly outlined for systems involving hydrogen bond associations. Improvements should come by either increasing the strength of association between refrigerant and absorbent, increasing the number of active sites which can combine, or combining donor and acceptor capability on the same molecule. Improvements will probably be most dramatic in the latter case, and might come with refrigerants such as difluoramine (HNF_2) or dichloracetonitrile (Cl_2CHCN). Examples have been cited in the literature where strong molecular associations between DMF or dimethylsulfoxide (DMSO) and HNF_2 were attributed possibly to bonding of the type



which is similar to the structure proposed earlier. Although not as strongly, HNF_2 is believed to associate with acetonitrile by forming the structure $CH_3CN....H-N\genfrac{}{}{0pt}{}{F}{F}$. Infrared investigations by Allerhand and Schleyer revealed that the C-H stretching frequency in Cl_2CHCN shifted more than three times that in ClHC=CHCl when each compound was combined with DMSO. The significance of this finding as related to association of these two compounds remains to be determined.

The infrared spectrograph is a valuable tool for studying molecular mechanisms, but it has its limitations. Sometimes infrared spectral bands are very broad and diffuse due to complicated stretch and rotational interactions with the molecule. A more frequent limitation is that the bands of specific interest overlap with bands from another species present in the system. It was thought ultrasonic spectra would provide valuable structural information for this system since several workers have utilized ultrasonics as a tool for obtaining structural or kinetic information for systems not too dissimilar.

An attempt was made to adapt ultrasonic techniques for directly studying relative strengths or exchange rates of hydrogen bonds in various organic refrigeration systems. No hydrogen bond relaxations have been observed by us even though others report such observations with similar (maybe not similar enough) interactions. The reason we have not been successful may be that: 1) The relaxations take place outside of our observable frequency range; 2) The type of bonding being studied is too weak to be observed; 3) The proper combination of variables such as temperature, concentration, etc. has not been found to bring this type of relaxation into our frequency range.

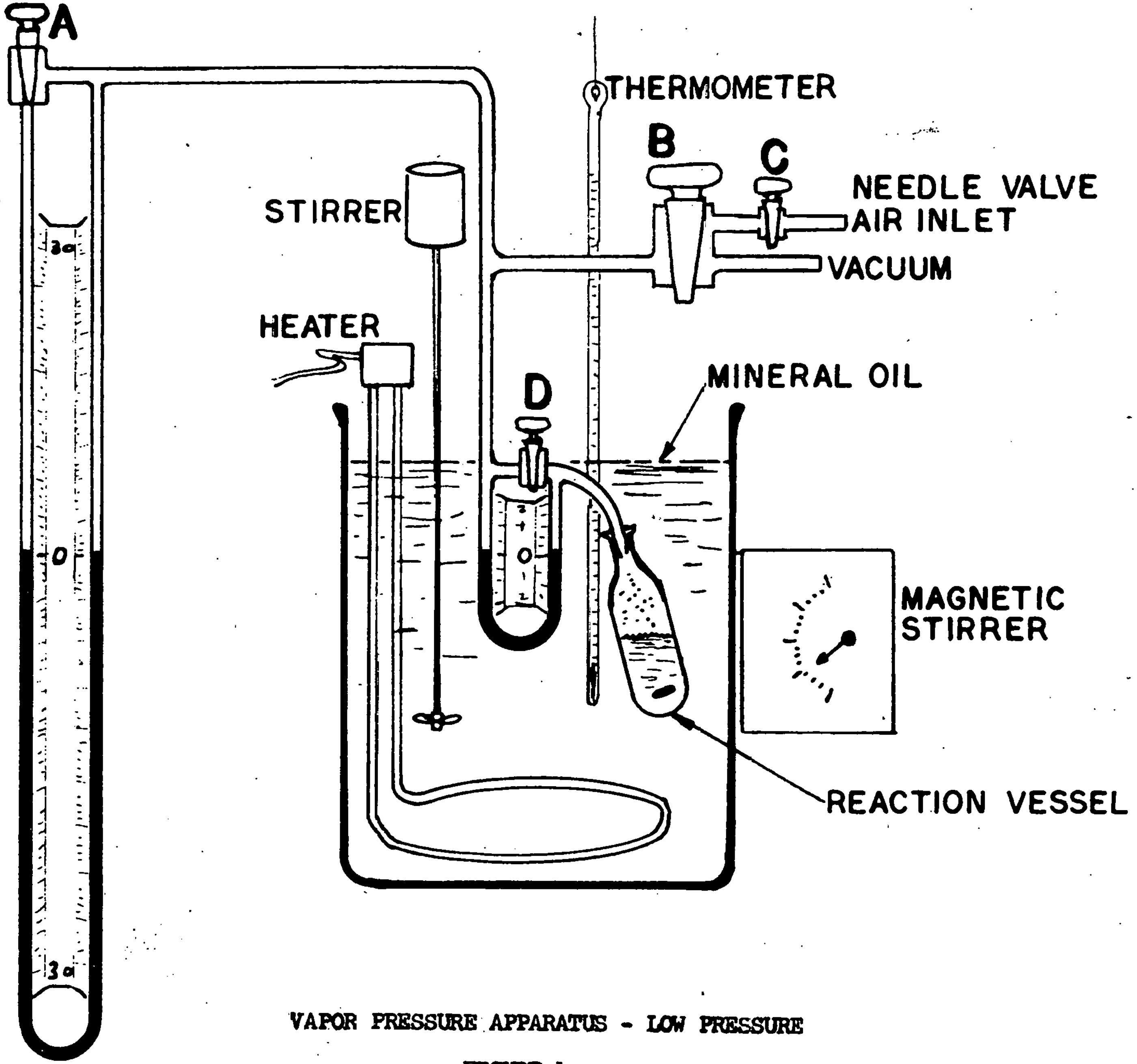
An indirect method for measuring bond strengths or rates of this type has shown some promise. Relaxations attributed to rotational isomerization about the C-C linkage have been observed in certain substituted ethanes, propanes, etc. When these compounds associate with another, such as a formamide, a certain amount of hindered rotation can be expected. This association may effect the rotation either kinetically or thermodynamically, both of which can be observed ultrasonically. The degree to which the rotational isomerization rate has been effected should be an indirect measure of the degree of association. We have observed these relaxations; however, the change of rate has been either too small to bear any significance or the relaxation has been too near the end of our spectrum range to be of value.

3-1 EXPERIMENTAL METHODS

The basic data collected for the evaluation of potential absorbent-refrigerant systems were vapor pressure-temperature curves for various concentrations of refrigerant in absorbent.

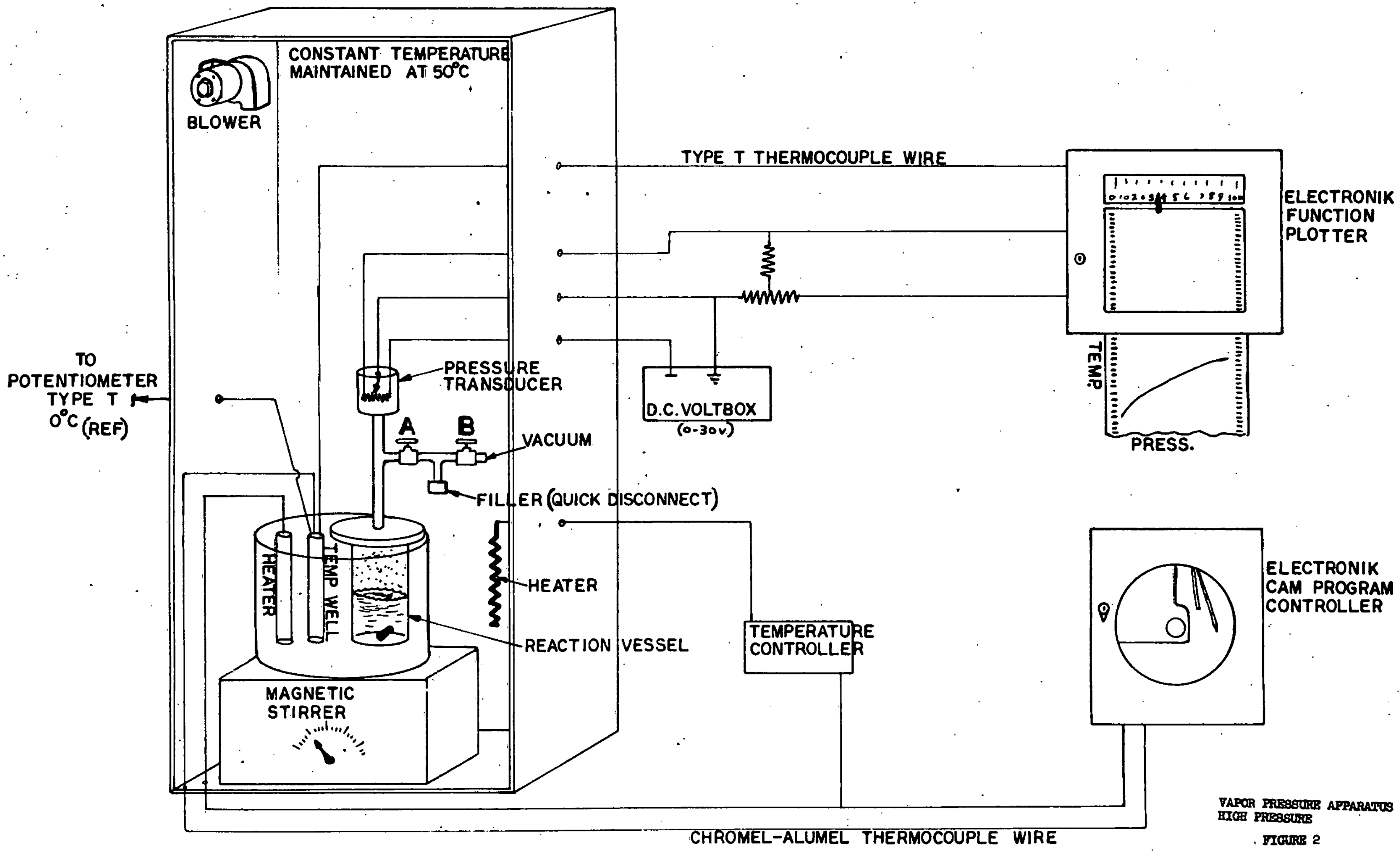
The liquid-liquid type apparatus is depicted in Figure 1. It was made of glass and used only when the solutions had very low vapor pressures at room temperature. The procedure for operation was as follows: The sample reaction vessel was disconnected from the apparatus, cleaned, and dried. It was weighed to within 0.0001 gram and then filled with about 5 to 10 ml of the high-boiling organic solvent to be tested. The lower boiling refrigerant was then added, and a solution was formed with a vapor pressure sufficiently low at room temperature so that accurate weighing was possible. The weight of the refrigerant was obtained by difference. The cell was then returned to the system and frozen in liquid nitrogen. Following adequate freezing, the cell was evacuated for several minutes by means of a vacuum pump. The vacuum valve "B" was then closed and the solution was allowed to melt with vigorous stirring. The solution was again frozen and degassed. Valve "B" was again closed to the pump and valve "D" was also closed above the reaction vessel. Valve "A" was always left closed following initial degassing of the large manometer. As the solution melted, air was introduced by reversing valve "B" and slowly cracking valve "C" in order to balance the solution manometer. The oil bath was then placed on the lab jack and the level adjusted so that all of the solution, both liquid and vapor, was maintained at a constant temperature. The oil bath temperature was slowly increased and the pressure was read directly from the large manometer after balancing the solution manometer. The temperature was read simultaneously from a mercury thermometer to within ± 0.1°C. The initial measurements proved conclusively that good agitation was necessary in the reaction vessel in order to obtain accurate pressure readings.

Figure 2 depicts a liquid-vapor automated device for recording pressure and temperature directly on an X-Y recorder. It was designed and built because most of the refrigerants of interest are gases with boiling



VAPOR PRESSURE APPARATUS - LOW PRESSURE

FIGURE 1



VAPOR PRESSURE APPARATUS - HIGH PRESSURE

FIGURE 2

points well below room temperature. The reaction vessel was constructed of aluminum with stainless steel valves and piping. The temperature axis recording the output of a copper-constantan thermocouple was calibrated against a potentiometer and the pressure axis recording the millivolt output from a pressure transducer was calibrated against a Seeger's pressure gauge with ± 0.05% F.S. reliability.

The procedure for filling the reaction vessell was as follows: The higher boiling organic solvent was weighed by difference to within ± 0.1 gram and introduced directly into the vessel. The vessel was then sealed and placed in an ice bath. Valves "A" and "B" were then opened and a vacuum of at least 20 microns was established. Valve "B" was then closed and the refrigerant cylinder was connected to the filler. The valve to the refrigerant cylinder was cracked, allowing small portions of refrigerant to be dispensed into the reaction vessel with a control of ± 0.1 gram. Subsequent runs could be made at a different concentration simply by adding more refrigerant to the reaction vessel. The temperature programmer was set so that the rise in temperature was 0.5°C/minute, and a safety circuit was installed so that a maximum pressure cutoff was established. This also allowed data to be plotted overnight without an operator.

The precision of the data in this investigation is generally within 0.5 psia for pressures below 30 psia, and within 1.0 psia for pressures between 30 and 100 psia. A Robinson-Halpern pressure transducer was employed to provide D.C. output to the pen (X-axis) and a type J thermocouple wire furnished the output to the chart drive (Y-axis). The overall precision in the form of Duhring plot was generally ± 1.0°C.

3-1.1 Other Measurements

Throughout this report there will be included other items of numerical information determined in our laboratories. Briefly, some of the methods used were: Heat of Dilution. An isothermal calorimeter, modeled after a design used by this author (WJB) in earlier studies(1) was built to

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(1) W. J. Biermann, et al. J. Am. Chem. Soc 74, 322 (1952), 76, 4289 (1954) Can. J. Chem. 34, 1591 (1956).

measure heats of dilution and heat capacity. This was used for results given in connection with cis, 1,2-dichloroethylene and N,N-dimethylalkamides. Specific Heat. Some specific heats were determined with a wide mouthed Dewar flask and heated copper block. The Dewar flask calorimeter is "calibrated" by filling with weighed water to the working depth and then adding a calculable amount of heat by rapidly moving a tared copper block from boiling water to the calorimeter flask. The water equivalent of the flask (and accessories) is the unknown in the heat balance. The method can, if done carefully, yield results of ± 2-3% accuracy. Heat Transfer Coefficients. Film side heat transfer coefficients for absorbers are key numbers in evaluating any potential absorption refrigeration system. In this program, we had access to two laboratory facilities which simulated horizontal and vertical absorber tubes. These facilities were used not only to measure the heat transfer coefficients of absorbers operating with novel chemical systems, but also to test the effectiveness of heat transfer additives in enhancing the film side heat transfer coefficient. Calculations were made using classical counterflow heat exchanger calculations and segregating the film coefficient by summing up individual resistivities to heat flow.

Data obtained from these laboratory facilities were completely consistent with heat transfer coefficients obtained in operating machines within the uncertainty of the scaling factors.

Miscellaneous. Concentrations as used in this section were generally obtained by careful weighing in making solutions. Temperatures were either from mercury in glass thermometers, with proper immersion, or from copper-constantan thermocouples. Calibration was against NBS calibrated platinum thermometers. Pressure sensors were calibrated against a dead weight gauge.

A set of Class M metric weights was kept for periodic calibration of precision balances.

In addition to observations of vapor pressure-temperature relationships, the programmed apparatus gave a method for provisional stability assessments. In cases where decomposition took place at a significant rate, which were not uncommon, displacement of successive T-P cycles gave visual warning of this.

3-2 SYSTEMS STUDIED

3-2.1 Refrigerants

In Table I has been assembled a list of those refrigerants which were candidate materials for this study. An asterisk has been used to designate those refrigerants for which numerical data have been included in this report. These generally comprise those refrigerants whose stability, physical properties and degree of interaction make them promising candidates and also those refrigerants whose structures are interesting in establishing trends. Generally speaking, data for refrigerants which were unstable, or whose properties do not place it in one of the above classes, have not been included.

3-3 ABSORBENTS

The primary functional group used for absorption was the amide group $-CO-NR_2$ where R is either H, which gives the lowest molecular weight, or methyl groups whose electropositive character enhances the basicity of the nitrogen atom. Fortunately since the earlier work done by Zellhoefer, et al., heavier disubstituted amides with higher boiling points have become available in commercial quantities. These materials, of the general formula $(CH_3)_2N\cdot CO\cdot C_nH_{2n+1}$ are available in relatively pure state for values of n up to 18. For purposes of this work, the n = 5 material, N,N-dimethylhexamide was chosen as the standard absorbent for this study. This is sufficiently non-volatile to require little or no rectification with the more promising halocarbon refrigerants. For purposes of comparison, a few systems were run with either N,N-dimethylformamide or with N,N-dimethyldodecamide in addition.

In an effort to reduce the molecular weight per functional unit, several difunctional absorbents were synthesized in small amount, namely:

N,N,N',N'-tetramethylmalonamide	$(CH_3)_2N-CO-CH_2-CO-N(CH_3)_2$ and
N,N,N',N'-tetramethylsuccinamide	$[(CH_3)_2N-CO-CH_2-]_2$

were prepared for test purposes.

Two additional absorbents of chemical simularity, 2-pyrrolidone and N-methyl-2-pyrrolidone, which are high boiling liquids and commercially available (GAF, 2-pyrol^{TM} and m-pyrol^{TM}) were evaluated with several of the more promising refrigerants.

Several other materials were found which were expected to show high basicity, two of which, trimethylphosphonoacetate, are also reported in this document, and tetraethylene glycol diethyl ether.

3-3.1 Absorbent Properties

The "standard" absorbent used in this work was a commercial N,N-dimethylhexamide [$(CH_3)_2N-CO-C_5H_{11}$] marketed by C. P. Hall Company of Chicago, Illinois under the trade name of "Hallcomide." Various members of this series are available and are designated by the number of carbon atoms in the chain; i.e., N,N-dimethylhexamide is M-6, which abbreviations are used in later presentations of data.

Some of the key properties of M-6 are listed below, obtained variously from the manufacturer or from our own measurements.

Hallcomide M-6

Chemical Names: N,N-dimethylhexamide; N,N-dimethylcaproamide

Approximate Molecular Weight	143
Boiling Range (400 Pa)	83-89°C
Freezing Point	-40°C
Flash Point	88°C
Fire Point	98°C
Density	889 kg/m^3
Viscosity (25°C)	0.002 Pa-s
Specific Heat (35°C)	2.21 kJ/kg
% N,N-dimethylamide	95%
Miscibility Limits, Water at 20°C	0-13% Water

The Hallcomides are mildy irritating to the skin, not volatile enough to constitute an inhalation hazard and are similar in toxicity to mineral oil or turpentine if administered parenterally.

The N,N dialkylamides are stable at 200°C for long periods of time, are highly resistant to hydrolysis by water and tend to be highly effective solvents for elastomers and resins. Polyethylene, nylon and Teflon are acceptable gasketing materials, butyl rubber being marginal.

Figure 3 shows the variation of normal boiling point for the N,N dimethylamide series compared to methyl and ethyl esters of the aliphatic acids and to the unsubstituted amides.

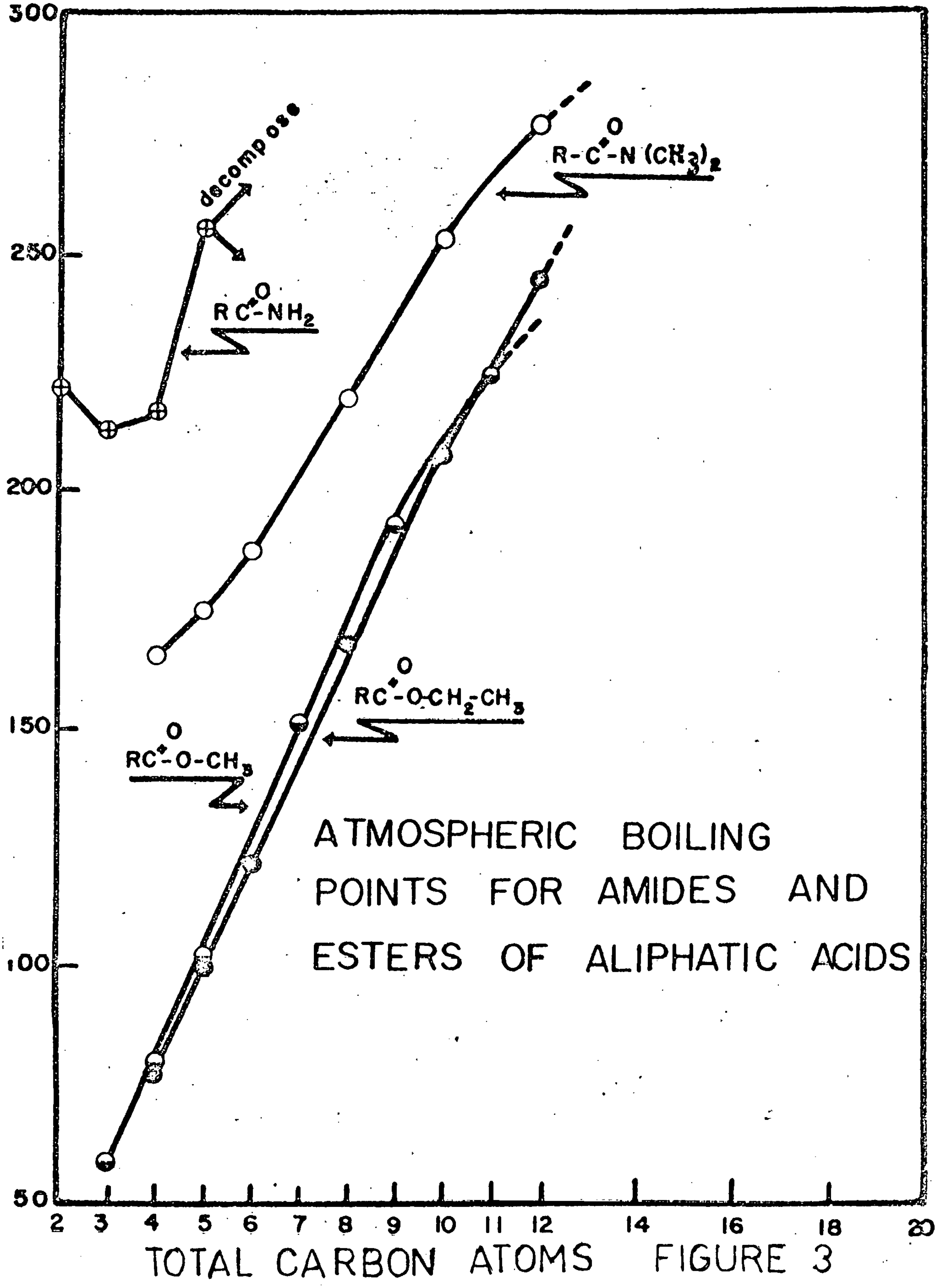
TABLE I

REFRIGERANTS CONSIDERED IN THIS STUDY

Number	Formula	Boiling Point, °C	Pressure kPa at 4.5°C	Pressure kPa at 48.9°C	Heat of Vapor kJ/kg-°K
11	CCl_3F	23.7	48.5	579	195 (at -15°C)
12	CCl_2F_2	-29.8	357	1191	158 (at B.P.)
13	$CClF_3$	-81.4	2203	3870	148 (-30°C)
14	CF_4	-127.9			144 (Trouton)
21*	$CHFCl_2$	8.9	850	384	253.8 (15.5°C)
22*	CHF_2Cl	-40.8	574	1893	216.3 (30.0°C)
23	CHF_3	-82.1	2827	6895	237 (Trouton)
30	CH_2Cl_2	39.8	23.2	136.5	315 (30°C)
31	CH_2ClF	-8.9			339 (30°C)
32	CH_2F_2	-51.7	931	3103	376 (Trouton)
40	CH_3Cl	-11.8	303	1048	416 (30°C)
41	CH_3F	-78.3			501 (Trouton)
50	CH_4	-162.2			610 (30°C)
111	$CCl_3 \cdot CCl_2F$	137.0			163 (Trouton)
112a	$CCl_2F \cdot CCl_2F$	92.8	3.4	22.	156 (30°C)
113a	$CClF_2 \cdot CCl_2F$	47.6	18.6	103	163.9 (30°C)
114a	$CClF_2 \cdot CClF_2$	3.6	103	441	143.9 (30°C)
115	$CClF_2 \cdot CF_3$	-38.7	501	1623	125.8 (30°C)
116	$CF_3 \cdot CF_3$	-78.2	2070.	5500	128 (Trouton)
120	$CHCl_2 \cdot CCl_3$	162.2			188 (Trouton)
121	$CHCl_2 \cdot CCl_2F$	117			183 (Trouton)
122*	$CHFCl \cdot CCl_2F$	72			180 (Trouton)
123b*	$CF_3 \cdot CHCl_2$	27.8	41	179	137 (30°C)
124a	$CHF_2 \cdot CClF_2$	-9.7	179.7	714	169.7 (30°C)
125	$CF_3 \cdot CF_2Cl$	-12.8			234 (Trouton)
130c	$CH_2Cl \cdot CCl_3$	146			218 "
131c	$CH_2F \cdot CCl$.	102.8			218 "
132c	$CH_2F \cdot CFCl_2$	17.2			216 "
133a*	$CHF_2 \cdot CHFCl$	5.8			215
134c	$CH_2F_2 \cdot CF_2Cl$	-23			215
140a	$CH_2Cl \cdot CHCl_2$	113			188
141a	$CH_2Cl \cdot CHClF$	73.9			260
142a*	$CH_2F \cdot CHCLF$	35			269
142b*	$CH_2Cl \cdot CHF_2$	-9.4	83	345	216 (30°C)
143a	$CH_2F \cdot CHF_2$	5			290 (Trouton)
150a	$CH_2Cl \cdot CH_2Cl$	83.9			316 "
151a	$CH_2F \cdot CH_2Cl$	35			327 "
152a	$CH_2F \cdot CH_2F$	-25			330 "

TABLE I (cont'd.)

Number	Formula	Boiling Point, °C	Pressure kPa		Heat of Vapor kJ/kg-°K
			at 4.5°C	at 48.9°C	
160	CH_3CH_2Cl	13.3			390 (Trouton)
161	CH_3CH_2F	-37			432 "
170	$CH_3 \cdot CH_3$	-89			538 "
217	C_3F_7Cl	$\simeq$5.8	138	510	153 "
318	C_3F_8	-6.05	152.6	634.8	107 "
500	Azeotrope	-2.22	450.2	475.8	195.7 (30°C)
502	Azeotrope	-45	654	2034	159.8 (30°C)
	$CFCl{:}CFCl$*				
	cis $CHCl{:}CHCl$*				
	$CF_2Cl \cdot CF_2Cl$*				
	$CCl_2F \cdot CCl_2F$*				
	$CCl_2{:}CClH$*				
	$CCl_2{:}CClF$*				
	$CHBr{:}CHBr$*				
	$CH_2Cl \cdot CCl_2H$*				
	$CCl_2{:}CCl_2$*				
	$CHCl_2{:}CHCl_2$*				
	$CCl_3 \cdot CH_2F$*				
	$HCF_2 \cdot CCl{:}CHCl$*				
	$Cl_2C{:}CCl \cdot CF_3$*				
	$CFBr{:}CFBr$*				
	$CBr_2{:}CBrH$*				
	$HCF_2 \cdot CCl{:}CClH$*				
	CCl_4				



ATMOSPHERIC BOILING POINTS FOR AMIDES AND ESTERS OF ALIPHATIC ACIDS

FIGURE 3

4-0 RESULTS AND CALCULATIONS

In this report, solutions will be characterized by weight percentage of absorbent. In this convention, a "strong" solution is one with a high percentage of absorbent, hence weak in refrigerant.

Experimental data are generally deficient in doing initial analyses of system performance, hence extensive use is made of two rules:

1. Heat capacity of solutions are assumed to be mole fraction weighted averages of the constituents:

$$Cp_{1,2} = \chi_1 Cp_1 + \chi_2 Cp_2$$

which would be true if the solution were "regular."

2. Hess' Law is extensively employed in obtaining energy balances in a component. In most cases this involves the use of accurately known heats of vaporization and "best guesses" for the smaller thermal effects due to heat of dilution and sensible heat transfer.

Refrigerant properties, where available, were taken from the ASHRAE Basic Data Manual. In many cases, the vapor pressure of refrigerants over a temperature range were measured and heats of vaporization approximated from Trouton's Law.

4-1.1 System: R21/Tetraethylene glycol dimethyl ether

In 1936, G. F. Zellhoefer(1) described a prototype absorption chiller at the annual meeting of the American Society of Refrigerating Engineers. This machine was based on the use of dichloromonofluoromethane (R-21) absorbed in the dimethyl ether of tetraethylene glycol and was designed to be operated on low pressure steam with heat to be rejected to cooling tower water at 29.4°C. This paper is a good starting place in the actual assessment of potential systems since it is one of the very few systems which has ever reached hardware.

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(1) J. of the A.S.R.E. p 317-320, May 1937.

A convenient way of presenting data is the use of the Duhring plot in which the temperature of a given solution is plotted as a function of the temperature of pure refrigerant at the same refrigerant vapor pressure. In most cases, a straight line relationship, within the accuracy with which solution vapor pressures are generally known, exists over a wide temperature range. The slope of each of these Duhring lines is approximately the ratio of the molar heat of vaporization from the solution to the molar heat of vaporization from pure refrigerant at similar partial pressures of vapor(1). Zellhoefer's presentation of vapor pressure data is in two sections; the higher concentration data are given as a series of isotherms plotting gauge vacuum against concentration, whereas the low concentration data are in the form of isobars, with temperature and concentration as axes.

When these data are collected in the form of a family of Duhring lines, as shown on the accompanying Figure 4, it is immediately evident that Zellhoefer's low and high concentration data are not consistent. This discrepancy is reflected in his discrepancy between theoretical and actual solution flows: (weak solution, theory 0.68 gpm/ton vs 0.90 gpm/ton, observed). For the purposes of this analysis, we will ignore this inconsistency, which tends to improve all predicted performance by a similar amount.

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(1) Haltenberger, W., Jr. Ind. Eng. Chem. 31, 783-786 (1939).

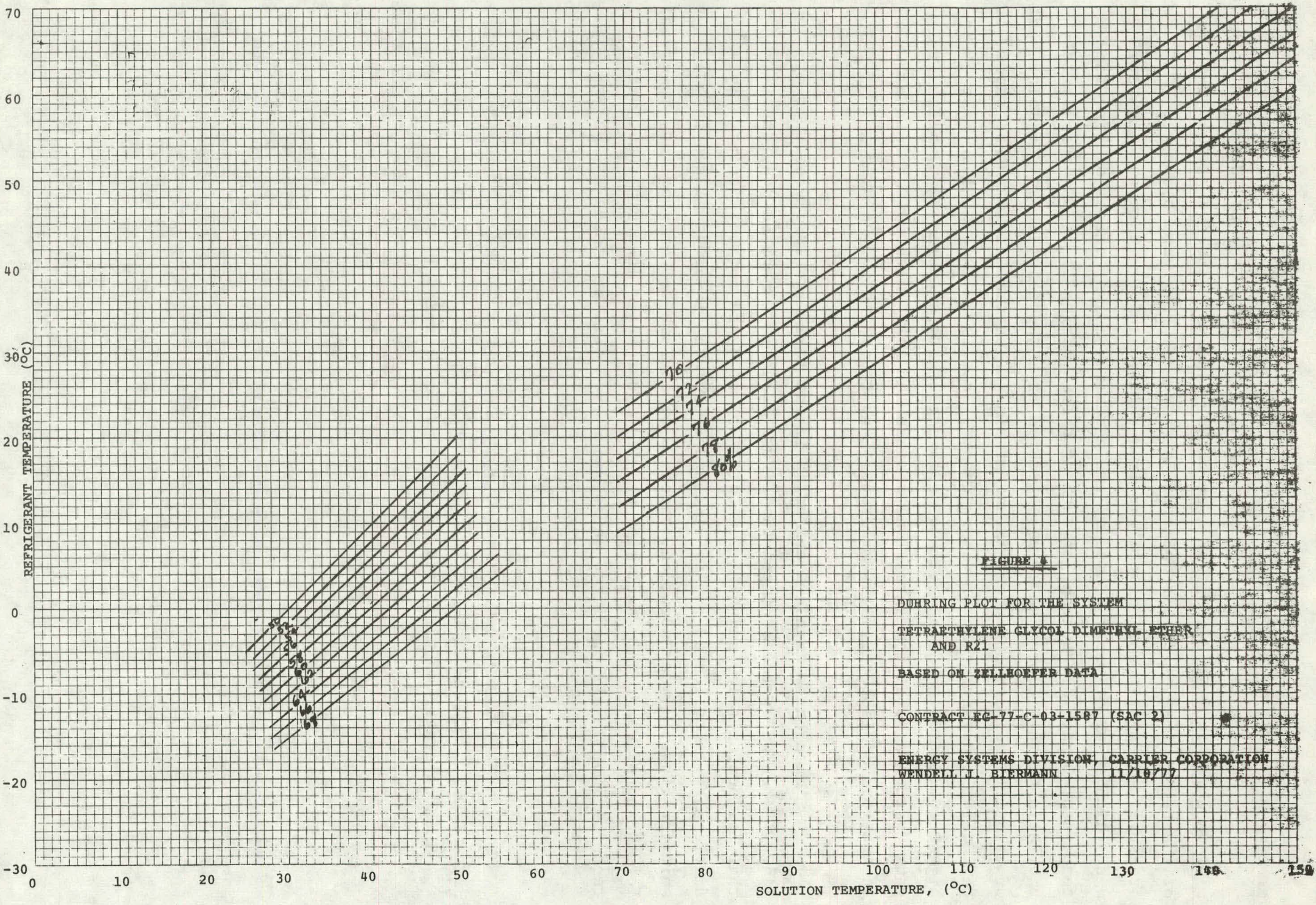


FIGURE 4

DUHRING PLOT FOR THE SYSTEM

TETRAETHYLENE GLYCOL DIMETHYL ETHER
AND R21

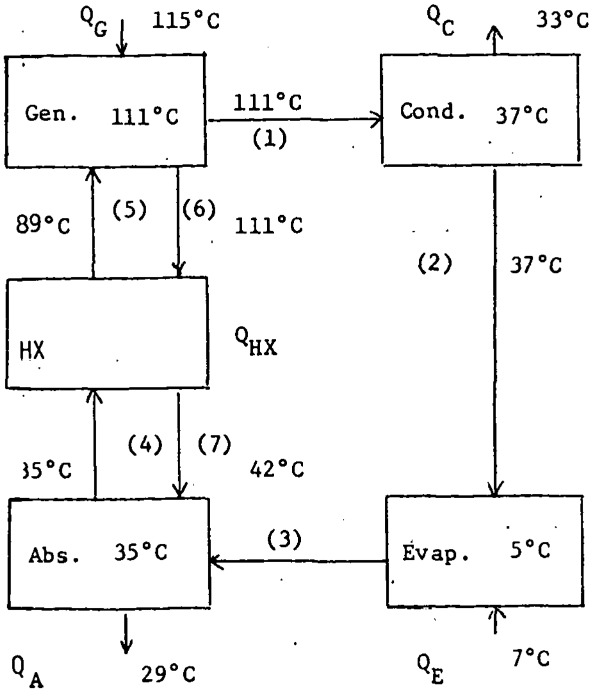
BASED ON ZELLHOEFER DATA

CONTRACT EG-77-C-03-1587 (SAC 2)

ENERGY SYSTEMS DIVISION, CARRIER CORPORATION
WENDELL J. BIERMANN 11/10/77

4-1.1.1 System R21, Tetraethylene glycol dimethyl ether

Water Cooled
Conditions



1. Superheated Ref. Vapor
2. Liquid Refrigerant
3. Saturated Ref. Vapor
4. Weak Sol. to HX
5. Weak Sol. to Gen.
6. Strong Sol. to HX
7. Strong Sol. to Abs.

No rectifier needed. Neglect thermal effects of generator liquid bleed stream and condenser vapor purge stream.

Point	Temp. °C	[X] Wt % abs.	W kg/kg-ref.	h kJ/kg	Wh kJ/kg-ref	Pressure kPa	Dew Pt °C	Q kJ/kg-ref	Q'(Q_E=10kW) kg/hr ref
1	111	0	1	350	350	269	37	Q_A = 264	12.7
2	37	0	1	78.9	78.9	269	37	Q_E = 208	10
3	7	0	1	287	287	85.5	5	Q_G = 286	13.8
4	35	50.0	2.72			85.5	5	Q_C = 248	11.9
5	89	50.0	2.72			269	37	Q_{HX} = 201	9.66
6	111	79.0	1.72			269	37		
7	42	79.0	1.72			85.5	5	COP = Q_E/Q_G =	73%

Analysis Based on Zellhoefer Conditions, as reported.

Heat Exchanger:

Strong Stream Q_{max} = (111 - 35) x 1.72 x Cp (79%) = 222 kJ/kg ref.

HX Efficiency = (111 - 42)/(111 - 35) = 91%

Q_{HX} = 201 kJ/kg ref.

4-1.1.1 System R21, Tetraethylene glycol dimethyl ether (cont'd.)

$$\mathcal{X}_2\ (79\%) = \frac{0.79/242}{0.79/242 + 0.21/103} = 0.62 \text{ mole fraction absorbent}$$

$$\mathcal{X}_2\ (50\%) = \frac{0.50/242}{0.50/242 + 0.50/103} = 0.30 \text{ mole fraction absorbent}$$

$$Cp\ (79\%) \cong (0.62 \times 2.15 + 0.38 \times 1.08) = 1.73 \text{ kJ/kg-°K}$$

$$Cp\ (50\%) \cong (0.30 \times 2.15 + 0.70 \times 1.08) = 1.40 \text{ kJ/kg-°K}$$

$$W \text{ (strong)} = 0.50/(0.79 - 0.50) = 1.72 \text{ kg/kg refrigerant}$$

$$W \text{ (weak)} = 0.79/(0.79 - 0.50) = 2.72 \text{ kg/kg refrigerant}$$

$$Q_A = \underbrace{[h_{\ell}\ (35°) - h_{v}\ (5°)]}_{-208} + \underbrace{\Delta H_{dil}}_{-35} + \underbrace{1.72\ [Cp\ (79\%) \times (42 - 35)]}_{-21}$$

$$= 264 \text{ kJ/kg refrigerant circulated.}$$

$$Q_E = [h_{v}\ (35°) - h_{\ell}\ (37°)] = 208 \text{ kJ/kg refrigerant circulated.}$$

$$Q_G = \underbrace{\Delta H_{dil}}_{35} + \underbrace{[h_{v}\ (111°) - h_{\ell}\ (111°)]}_{167} + \underbrace{2.72\ [Cp\ (50\%) \times (111 - 89)]}_{84}$$

$$= 286 \text{ kJ/kg refrigerant circulated.}$$

$$Q_C = h_{\ell}\ (37°) - h_{v}\ (111°, 85 \text{ kPa})$$

$$- 248 \text{ kJ/kg-ref.}$$

$Q_A/Q_E = 1.27$ $Q_G/Q_E = 1.38$ $Q_C/Q_E = 1.19$

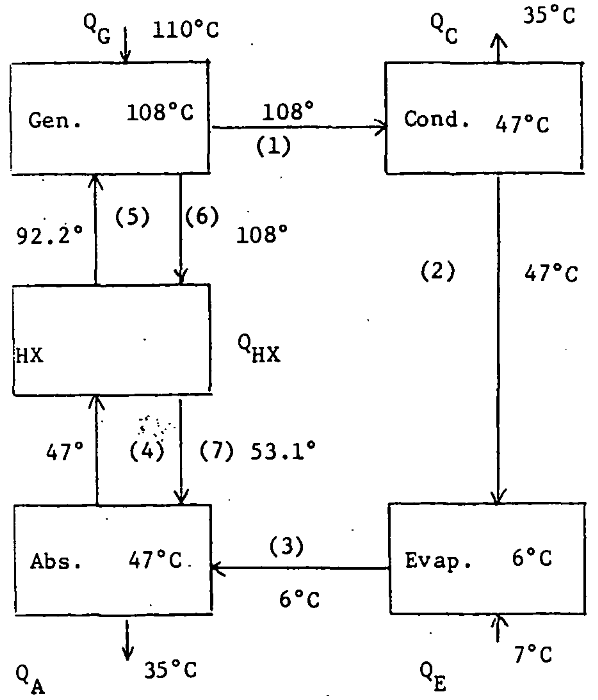
$Q_{HX}/Q_E = 0.97$

$$Q_{pump} = \frac{173 \times 2.72}{3600 \times \text{density}} \times \frac{(269 - 86) \times 1000}{\text{Efficiency}} \approx 50 \text{ watts}$$

assuming density = 1000 kg/m^3, eff = 50%.

4-1.1.2 System R21/Tetraethylene glycol dimethyl ether

Air Cooled
Conditions



1. Superheated Ref. Vapor
2. Liquid Refrigerant
3. Saturated Ref. Vapor
4. Weak Sol. to HX
5. Weak Sol. to Gen.
6. Strong Sol. to HX
7. Strong Sol. to Abs.

No rectifier needed. Neglect thermal effects of generator liquid bleed stream and condenser vapor purge stream.

Point	Temp. °C	[X] Wt % abs.	W kg/kg-ref.	h kJ/kg	Wh kJ/kg-ref	Pressure kPa	Dew Pt °C	Q kJ/kg-ref	Q'(Q_E=10kW 184kg/hr ref
1	108	0	1	355	355	364	47	Q_E 196	10.0
2	60	0	1	90	90	364	47	Q_C 265	13.5
3	47	0	1	286	286	91	6	Q_A 240	12.2
4	47	62.8	8.65			91	6	Q_G 467	23.9
5	92.2	62.8	8.65			364	47	Q_{HX} 684	34.9
6	108	71.0	7.65			364	47		
7	53.1	71.0	7.65			91	6	COP = 0.42	

$$\chi_2\ (71.0\%) = \frac{0.71/242}{0.71/242 + 0.29/103} = 0.51 \text{ mole fraction absorbent}$$

$$\chi_2\ (62.8\%) = \frac{0.628/242}{0.628/242 + 0.372/103} = 0.42 \text{ mole fraction absorbent}$$

Cp (71.0%) = (2.15 x 0.51 + 1.08 x 0.49) = 1.63 kJ/kg-°K

Cp (62.8%) = (2.15 x 0.628 + 1.08 x 0.372) = 1.75 kJ/kg-°K

4-1.1.2 System R21/Tetraethylene glycol dimethyl ether (cont'd.)

Strong Stream $Q_{max} = (108 - 47) \times 1.63 \times 7.65 = 760$ kJ/kg refrig.

Assume 90% Efficient Heat Exchanger

$Q_{HX} = 760 \times 0.90 = 8.65 \times 1.75 \times (t_5 - 47)$

$t_5 = 92.2$

$0.90 = (108 - t_7)/(108 - 47)$

$t_7 = 53.1$

$$Q_A = \underset{(286\ -\ 90)}{h_\ell (47°) - h_v (6°)} + \underset{35}{\Delta H_{dil}} + \underset{76}{1.63\ (53.1 - 47) \times 7.65}$$

$Q_A = 307$ kJ/kg refrig.

$$Q_G = \underset{35}{\Delta H_{dil}} + \underset{(355\ -\ 162)}{[h_v (108) - h_\ell (108)]} + \underset{239}{8.65 \times 1.75 \times (108 - 92.2)}$$

$= 467$ kJ/kg refrig.

$Q_C/Q_E = 1.35$

$Q_A/Q_E = 1.22$

$Q_G/Q_E = 2.39$

$Q_{HX}/Q_E = 3.49$

$$Q_{pump} = \frac{184 \times 8.65}{3600 \times \text{density}} \times \frac{(364 - 91) \times 10^3}{\text{Efficiency}}$$

$Q_{pump} = 241$ watts (density $\approx$ 1000 kg/m^3; eff = 50%).

4-1.1.3 Comments, Tetraethylene Glycol Dimethyl Ether (R-21)

For the water cooled case, the calculated COP is about 0.73 vs the observed machine efficiency of 0.53. The discrepancy is mostly in the inconsistency of the vapor pressure data which is in such a direction as to enhance efficiency by projecting a larger concentration difference between strong and weak streams than would be the experience. We have also ignored small losses due to rectification, bleed streams, losses to the surroundings which are very small compared to other uncertainties in the calculation.

Our primary interest in this comparison is the difference between a water cooled and an air cooled system. The most important points that emerge are:

Concentration Change. In the water cooled case the strong stream enters the absorber at 79% and leaves at 50%, and only 2.72 kg of weak solution need be circulated per kg of refrigerant circulated, or for a 10 kW cooling load, the pump rate is 471 kg per hour, with an electric power consumption in the neighborhood of 50 watts. Because of the higher temperatures at which air cooled condenser and absorber will operate, the circulation rate of the weak fluid now increases to 8.65 kg/kg refrigerant or 1592 kg/hour weak solution for the same 10 kW cooling load. The pump power increases to 241 watts. This need for increased flow rate is at the root of most limitations to air cooled cycles using low latent heat refrigerants.

Heat Exchanger. Keeping the same 90% heat exchanger efficiency we note that the ratio of sensible heat transferred here to the cooling produced increases from 0.97 to 3.49 in going from water cooling to air cooling. Even so, this heat exchanger is still too small since examination of the increased generator load shows that essentially all the increased load is due to the sensible heat losses in heating up the entering weak solution stream.

It is evident that so long as Q_E per kilogram of circulated refrigerant is small, keeping the ratio of Q_{Gen}/Q_E small will require enormous amounts of heat transfer surface in order to keep Q_{HX}/Q_E high. Other heat exchangers can also be used; for example, cold refrigerant gas leaving the evaporator can be used to cool entering liquid refrigerant from the condenser, thus reducing the sensible heat losses in flashing the warm entering liquid down to the pressure of the evaporator-absorber section. This will increase the Q_E per pound of refrigerant circulated but will also increase the absorber load.

Streams (1) and (5), weak solution entering the generator and the hot leaving vapor can also be put into heat exchange to reduce the generator losses in sensible heat to the entering liquid.

Overall. If we compare the loads on the individual components for air and water cooled machines supplying 10 kW cooling:

	R-21/TGME*		
	Water Cooled	Air Cooled	Water Cooled Lithium Bromide
Evaporator	10 kW	10 kW	10 kW
Condenser	11.9	13.5	10.6
Absorber	12.7	12.2	12.5
Generator	13.8	23.9	13.2
Solution HX	9.7	34.9	5.02

---

* These results, please recall, are based on inconsistent vapor pressures which significantly favor the R-21/TGME system.

4-1.2 cis 1,2-dichloroethylene/N,N dimethyldodecamide (M-12)

The vapor pressure of cis 1,2 dichloroethylene was measured in the same method as described for solutions. Numerical data are collected in Table 2 and were found to be accurately described by the equation (valid from 0 to 60°C refrigerant temperature)

$$\ell nP = \frac{-3749.1}{T} + 15.949$$

where P is in kiloPascals and T is in degrees Kelvin.

A series of 1,2 dichloroethylene solutions in M-12 were prepared by weighing on an analytical balance to within a few tenths of a milligram and the raw data presented in Table 3 were collected. The data for 87.00% and 90.00% M-12 solutions were taken in a vertical absorber test apparatus in connection with film heat transfer coefficient measurements and are in good agreement with the results taken in the direct manometric method.

It was found that the vapor pressure-temperature relationship for each concentration could be represented analytically (average deviation between equation and data points < 1°C) by means of a Duhring equation of the form:

$$T_{refrigerant} = T_{solution}\ m(x) + b(x)$$

where m(x) and b(x) are empirically determined constants whose numerical value is a function only of concentration (x). Table 4 contains a listing of these constants as determined by least squares fitting on data from Table 4. $T_{refrigerant}$ is a measure of the partial pressure of refrigerant over the solution and is derived from the empirical vapor pressure-temperature relationship given above.

The constants m(x) and b(x) were found to be closely described by the equations:

$$m(x) = 1.1274 - 0.004833[x]$$

$$b(x) = -87.89 + 2.143[x] - 0.0177[x]^2$$

where [x] is the concentration of M-12 in weight percentage.

Combining these equations, we conclude that the temperature (t_{ref}) at which pure refrigerant would show the same vapor pressure as a solution of [x] weight percent concentration M-12 at a temperature T_{sol} can be expressed by:

$$T_{ref} = [1.1274 - 0.004833(x)]\ T_{sol} - 87.89 + 2.143(x) - 0.0177(x)^2$$

Figure 5 is a series of Duhring plots which are the loci of this equation for various values of (x) in the region of interest.

In addition to the vapor pressure data, calorimetric data for the heat of mixing of cis 1,1 dichloroethylene and M-12 in various ratios were measured and the resultant (smoothed) data are presented in Figure 6.

The specific heat of M-12 was determined to be:

$$C_{M-12} = 2.1 + (4t \times 10^{-3})\ \mathrm{kJ/kg\text{-}°K}$$

where t is the liquid temperature in degrees Celsius.

The specific heat of cis 1,2-dichloroethylene was measured and is 1.105 kJ/kg-°K.

Specific heats of solutions is obtained by Hildebrand's mole fraction weighting method.

TABLE 2

Vapor Pressures of cis 1, 2 Dichloroethylene Laboratory Results

Temperature (°C)	Pressure (inches of Hg)
0.0	2.67
2.5	3.08
5.0	3.47
7.5	3.93
10.0	4.42
12.5	4.98
15.0	5.59
17.5	6.27
20.0	6.97
22.5	7.83
25.0	8.77
27.5	9.74
30.0	10.85
32.5	12.00
35.0	13.22
37.5	14.60
40.0	15.90
42.5	17.39
44.0	18.34
45.0	19.18
46.0	19.90
47.0	20.45
48.0	21.23
49.0	21.93
50.0	22.67
51.0	23.36
52.0	24.20
53.0	25.00
54.0	25.70
55.0	26.45
57.5	28.38
58.6	29.40

TABLE 3

Vapor Pressures of Solutions of cis 1, 2 - Dichloroethylene in M-12 at Various Temperatures - Laboratory Results

94.49% M-12		92.67% M-12		76.96% M-12		66.67 ut % M-12	
T (°C)	P (in Hg)	T (°C)	P (in Hg)	T (°C)	P (in Hg)	T (°C)	P (in Hg)
20.6	0.40	25.0	0.50	25.00	1.67	25.0	2.55
25.0	0.42	30.0	0.70	30.0	2.04	30.0	3.10
30.0	0.60	35.0	0.90	35.0	2.59	35.0	3.90
35.0	0.78	40.0	1.12	40.0	3.20	40.0	4.85
40.0	0.96	45.0	1.36	45.0	3.94	45.0	5.90
45.0	1.15	50.0	1.70	50.0	4.78	50.0	7.10
50.0	1.41	55.0	2.15	55.0	5.80	55.0	8.60
55.0	1.75	60.0	2.60	60.0	6.96	60.0	10.25
60.0	2.12	65.0	3.10	65.0	8.38	65.0	12.20
65.0	2.60	70.0	3.68	70.0	9.75	70.0	14.35
70.0	3.05	75.0	4.40	75.0	11.58	75.0	16.80
75.0	3.68	80.0	5.20	80.0	13.80	80.0	19.60
80.0	4.40	85.0	6.18	85.0	15.80	85.0	22.40
85.0	5.15	90.0	7.15	90.0	18.04	90.0	25.75
90.0	6.00	95.0	8.21	95.0	21.25	95.0	29.45
95.0	7.00	100.0	9.40	100.0	23.84		
100.0	8.00	102.5	10.10	105.0	26.83		
105.0	9.20	105.0	10.85	107.0	28.44		
110.0	10.55	107.5	11.60	108.0	29.37		
112.5	11.20	110.0	12.40				
115.0	11.95	112.5	13.27				
120.0	13.60	115.0	14.00				
125.0	15.40	120.0	16.00				
130.0	17.30	125.0	18.10				
135.0	19.20	130.0	20.20				
140.0	21.70	135.0	22.60				
145.0	24.00	140.0	25.25				
150.0	26.40	145.0	28.00				
155.0	29.10						

TABLE 3 (cont'd.)

cis 1, 2 Dichloroethylene in M-12

30.00% M-12		91.77% M-12		95.20% M-12		79.65% M-12	
T (°C)	P (in Hg)	T (°C)	P (in Hg)	T (°C)	P (in Hg)	T (°C)	P (in Hg)
19.0	5.30	25.0	0.44	35.0	0.68	25.0	0.95
22.5	6.02	30.0	0.57	40.0	0.80	30.0	1.26
25.0	6.70	35.0	0.63	45.0	0.94	35.0	1.60
30.0	8.18	40.0	0.77	50.0	1.07	40.0	2.03
35.0	10.22	45.0	0.95	55.0	1.21	45.0	2.52
40.0	12.20	50.0	1.25	60.0	1.47	50.0	3.08
45.0	14.89	55.0	1.46	70.0	2.00	55.0	3.78
50.0	17.81	60.0	1.80	75.0	2.41	60.0	4.60
55.0	21.18	65.0	2.19	80.0	2.90	65.0	5.52
60.0	25.07	70.0	2.62	85.0	3.35	70.0	6.47
62.5	27.21	75.0	3.07	90.0	3.81	75.0	7.61
65.0	29.60	80.0	3.58	95.0	4.40	80.0	8.86
		85.0	4.27	100.0	5.17	85.0	10.00
		90.0	4.90	105.0	5.63	90.0	11.52
		95.0	5.62	110.0	6.45	95.0	13.44
		100.0	7.00	115.0	7.32	100.0	15.47
		105.0	8.00	125.0	9.93	105.0	17.66
		110.0	9.70	130.0	11.07	110.0	20.30
		115.0	11.16	135.0	12.40	115.0	23.18
		120.0	12.70	140.0	13.40	120.0	26.22
		125.0	14.38	145.0	15.67	125.0	29.90
		130.0	16.34	150.0	17.41		
		135.0	18.07	160.0	21.90		
		140.0	19.60	170.0	26.50		
		145.0	21.82				
		150.0	24.18				
		155.0	26.78				
		160.0	29.20				

TABLE 3 (cont'd.)

87.49 wt % M-12		82.68% M-12		89.39% M-12		85.45% M-12	
T (°C)	P (in Hg)	T (°C)	P (in Hg)	T (°C)	P (in Hg)	T (°C)	P (in Hg)
23.5	0.62	22.0	1.00	19.2	0.60	22.5	0.65
25.0	0.85	25.0	1.25	25.0	0.80	25.0	1.00
30.0	1.10	30.0	1.55	30.0	0.95	30.0	1.25
35.0	1.40	35.0	2.00	35.0	1.20	35.0	1.60
40.0	1.70	40.0	2.44	40.0	1.50	40.0	2.00
45.0	2.16	45.0	3.00	45.0	1.90	45.0	2.50
50.0	2.60	50.0	3.70	50.0	2.40	50.0	3.00
55.0	3.20	55.0	4.50	55.0	2.98	55.0	3.80
60.0	3.85	60.0	5.45	60.0	3.50	60.0	4.50
65.0	4.60	65.0	6.55	65.0	4.20	65.0	5.35
70.0	5.50	70.0	7.65	70.0	5.05	70.0	6.35
75.0	6.55	75.0	9.20	75.0	6.00	75.0	7.55
80.0	7.60	77.5	10.00	80.0	7.05	80.0	8.82
85.0	9.00	80.0	10.75	85.0	8.20	85.0	10.30
90.0	10.35	82.5	11.50	90.0	9.45	90.0	12.00
95.0	11.85	85.0	12.35	95.0	10.90	95.0	13.70
100.0	13.50	90.0	14.50	100.0	12.30	100.0	15.65
102.5	14.40	95.0	16.60	105.0	14.00	105.0	17.70
105.0	15.35	100.0	18.80	110.0	15.80	110.0	20.00
107.5	16.40	105.0	21.40	115.0	17.75	115.0	22.40
110.0	17.40	107.5	22.70	120.0	19.80	120.0	25.40
112.5	18.64	110.0	24.35	125.0	22.05	125.0	28.20
115.0	19.80	112.5	25.90	130.0	24.40	127.3	29.60
117.5	21.00	115.0	27.40	135.0	26.80		
120.0	22.20	117.5	29.40	140.0	29.35		
122.5	23.50						
125.0	25.90						
130.0	27.55						
134.0	30.00						

TABLE 3 (cont'd.)

cis 1, 2 Dichloroethylene in M-12

76.87% M-12		84.26% M-12		82.22% M-12		87.42% M-12	
T (°C)	P (in Hg)	T (°C)	P (in Hg)	T (°C)	P (in Hg)	T (°C)	P (in Hg)
25.0	1.30	20.0	0.78	25.0	1.07	40.0	1.40
30.0	1.66	25.0	0.94	30.0	1.32	45.0	1.62
35.0	2.06	30.0	1.15	36.5	1.83	50.0	2.04
40.0	2.64	35.0	1.46	40.0	2.04	55.0	2.52
45.0	3.23	40.0	1.84	45.0	2.47	60.0	3.00
50.0	3.93	45.0	2.24	50.0	2.82	65.0	3.62
55.0	4.68	50.0	2.70	55.0	3.45	70.0	4.33
60.0	5.63	55.0	3.32	60.0	4.05	75.0	5.02
65.0	6.68	60.0	3.85	65.0	4.97	80.0	6.00
70.0	7.96	65.0	4.68	70.0	5.76	85.0	6.94
75.0	9.39	70.0	5.40	75.0	6.77	90.0	8.08
80.0	10.89	75.0	6.45	80.0	7.98	95.0	9.52
85.0	13.00	80.0	7.34	85.0	9.12	100.0	10.95
90.0	16.04	85.0	8.68	90.0	10.47	105.0	12.23
95.0	18.54	90.0	10.08	95.0	12.07	110.0	14.01
100.0	20.65	95.0	11.83	100.0	13.93	115.0	15.10
105.0	23.23	100.0	13.42	105.0	15.40	120.0	16.77
110.0	26.03	105.0	14.95			125.0	18.80
115.0	29.17	110.0	17.23			130.0	20.62
116.0	29.84	115.0	19.64			135.0	22.57
		120.0	22.51			140.0	24.80
		130.0	28.98			145.0	27.20

TABLE 3 (cont'd.)

cis 1, 2 Dichloroethylene + M-12

90.00 wt % M-12	
30.0	0.80
35.0	1.15
40.0	1.40
45.0	1.75
50.0	2.15
55.0	2.60
60.0	3.20
65.0	3.80
70.0	4.50
75.0	5.32

87.00% M-12	
50.0	2.65
55.0	3.15
60.0	3.80
65.0	4.60
70.0	5.45
75.0	6.55

TABLE 4

Duhring Equation Constants for the System cis 1, 2 - Dichloroethylene/M-12

[X] Weight Percent M-12	m(x)	b(x)
87.49	.6979	-34.20
82.68	.7558	-30.93
89.39	.6624	-33.27
85.45	.7167	-32.45
94.49	.6652	-43.58
92.67	.6779	-40.92
76.96	.7922	-27.76
66.67	.8434	-21.99
30.00	.9541	- 4.62
91.77	.7090	-51.14
95.20	.5988	-47.11
79.65	.7242	-32.87
76.87	.7764	-31.22
84.26	.7034	-34.80
82.22	.7003	-33.44
87.42	.6513	-35.86
90.00	.7395	-41.45
87.00	.7706	-39.38

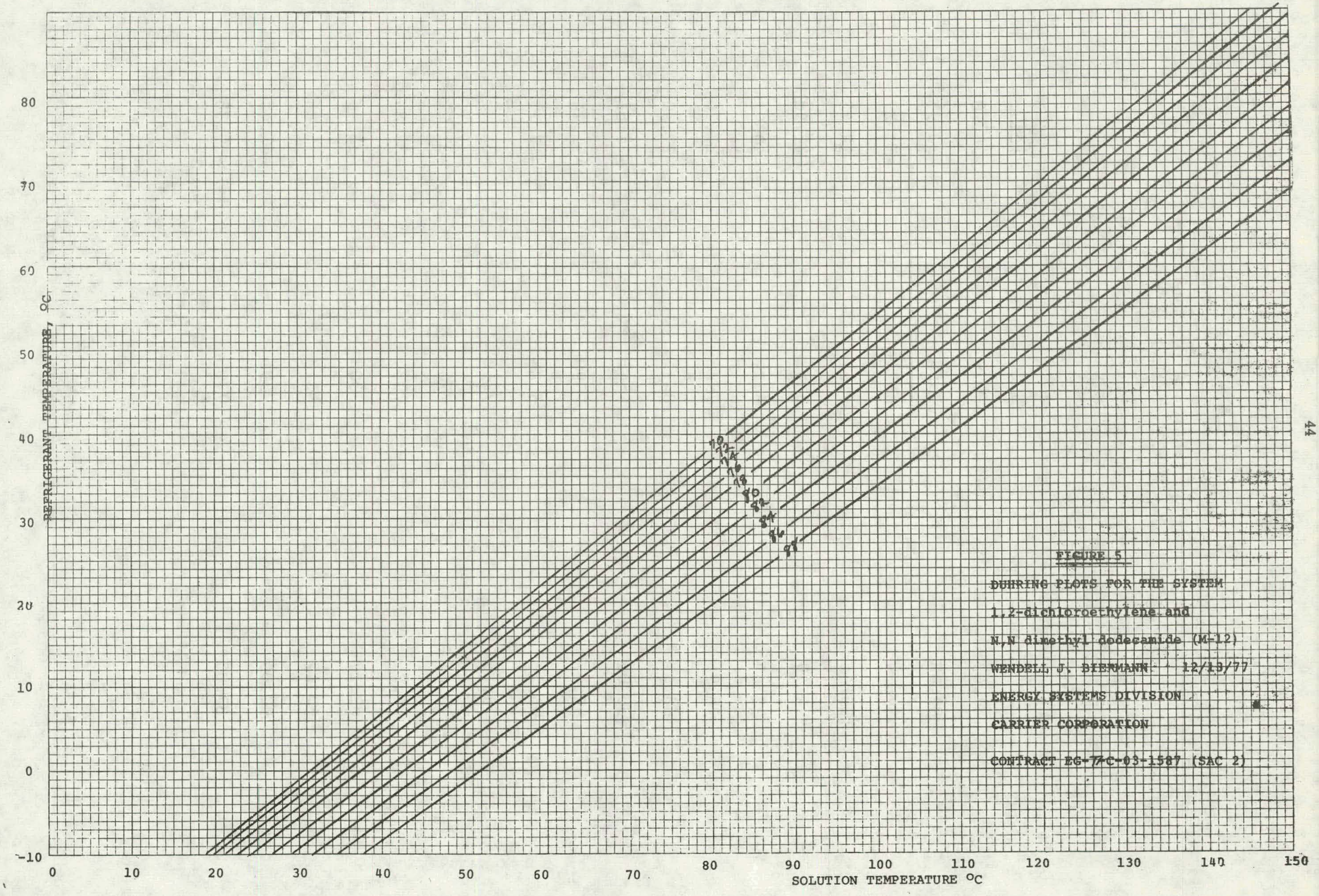


FIGURE 5

DUHRING PLOTS FOR THE SYSTEM

1,2-dichloroethylene and

N,N dimethyl dodecamide (M-12)

WENDELL J. BIERMANN 12/13/77

ENERGY SYSTEMS DIVISION

CARRIER CORPORATION

CONTRACT EG-77-C-03-1587 (SAC 2)

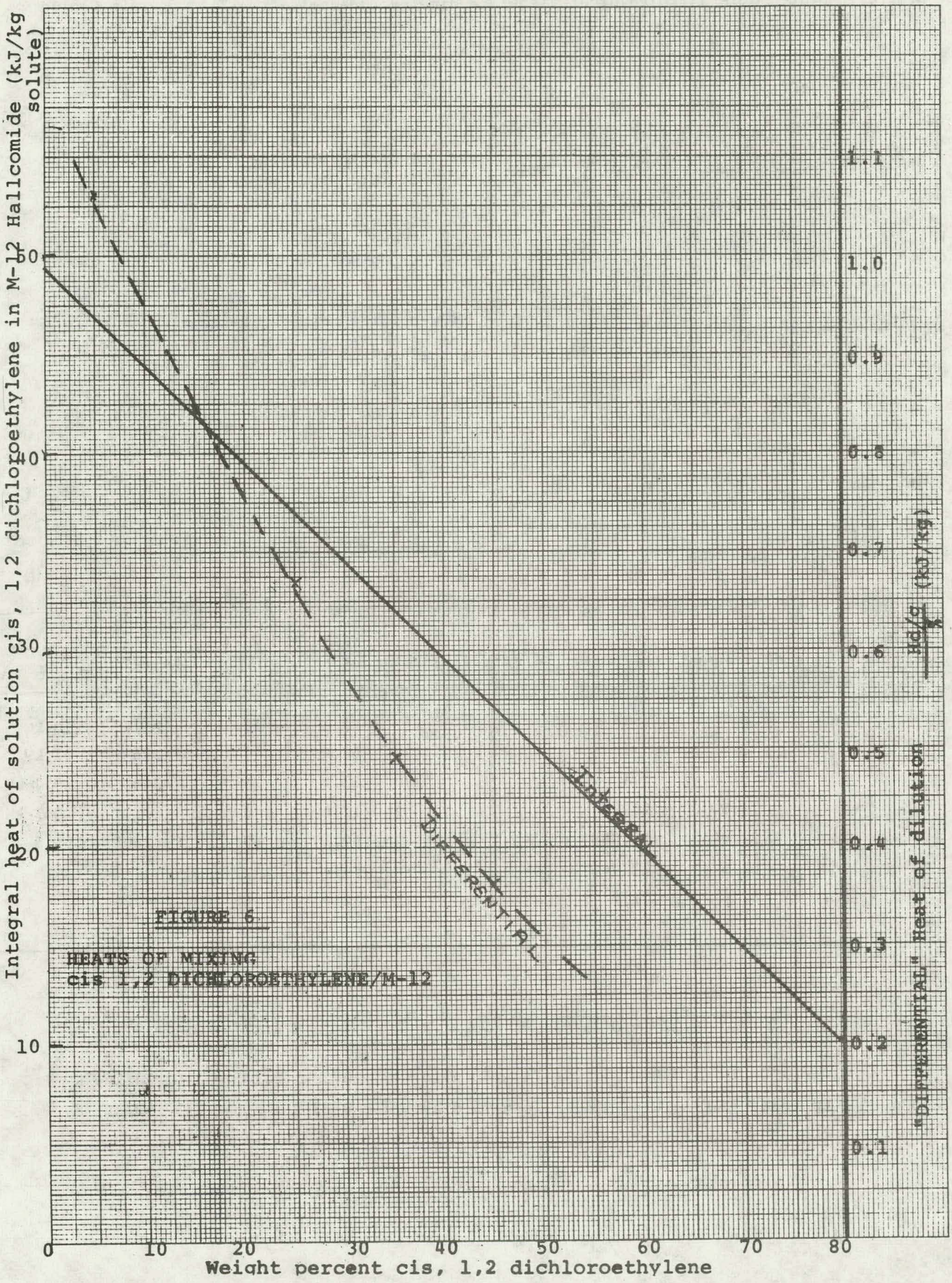
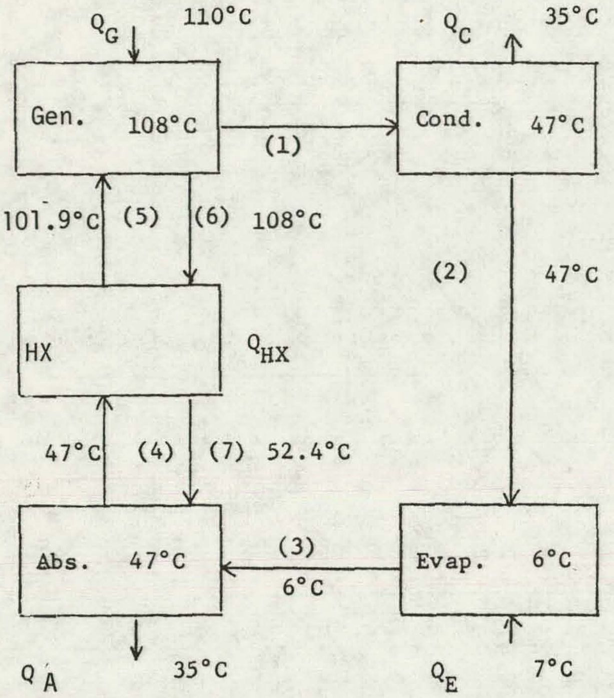


FIGURE 6

HEATS OF MIXING
cis 1,2 DICHLOROETHYLENE/M-12

4-1.2.1 System cis 1,2 dichloroethylene/N,N dimethyldodecamide (M-12) Air Cooled



1. Superheated Ref. Vapor
2. Liquid Refrigerant
3. Saturated Ref. Vapor
4. Weak Sol. to HX
5. Weak Sol. to Gen.
6. Strong Sol. to HX
7. Strong Sol. to Abs.

No rectifier needed. Neglect thermal effects of generator liquid bleed stream and condenser vapor purge stream.

Point	Temp. °C	[X] Wt % abs.	W kg/kg-ref.	h kJ/kg	Wh kJ/kg-ref	Pressure kPa	Dew Pt °C	Q kJ/kg-ref	Q'(Q_E=10kW 143kg/hr ref
1	108	0	1			69.4	47	Q_E = 251	10 kW
2	47	0	1			69.4	47	Q_A = 536	21 kW
3	6	0	1			12.4	6	Q_C = 343	10.4 kW
4	47	79.0	22.94			12.4	6	Q_G = 601	23.9 kW
5	101.9	79.0	22.94			69.4	47	Q_{HX} = 2405	95.8 kW
6	108	82.6	21.94			69.4	47		
7	52.4	82.6	21.94			12.4	6	COP = 42%	

$$x_2\ (79\%) = \frac{0.79/227}{0.79/227 + 0.21/97} = 0.62 \qquad x_2(82.6\%) = \frac{0.826/227}{0.826/227 + 0.174/97} = 0.67$$

$$Cp\ (79\%,\ 75°C) = 0.61\ [2.1 + (4 \times 75 \times 10^{-3})] + 0.38 \times 1.105 = 1.91\ kJ/kg\text{-}°K$$

$$Cp\ (83\%,\ 75°C) = 0.67\ [2.1 + (4 \times 75 \times 10^{-3})] + 0.33 \times 1.105 = 1.97\ kJ/kg\text{-}°K$$

Q_{max} (strong solution) = 21.94 x (108 - 47) x 1.97 = 2637 kJ/kg ref. cir.

Q_{max} (weak solution) = 22.94 x (108 - 47) x 1.91 = 26.73 kJ/kg ref. circ.

Assume HX is 90% efficient.

Q_{HX} = 0.90 x 2637 = 2405 kJ/kg ref. circulated

$$2405 = 22.94\ (t_5 - 47) \times 1.91$$

t_5 = 101.9°C

$$2405 = 21.94\ (108 - t_7) \times 1.97$$

t_7 = 52.4°C

ΔH_{vap} = T(17 + 0.011T) Nernst-Bingham Rule
= 6861 cal/g-MW = 296 kJ/kg at 59°C boiling point

Cp (vapor) $\cong$ 70% of Cp (liquid) $\cong$ 0.77 kJ/kg-°K

Q_C = sensible heat + latent heat
= 0.77 (108 - 47) + 296
= 343 kJ/kg ref. circulated.

Q_E = -1.105 (47-6) + 296
= 251 kJ/kg ref. circulated.

Q_G = sensible heat + latent heat + heat dilution
= 22.94 x 1.91 x (108 - 101.9) + 296 + 38
= 601 kJ/kg ref. circulated.

Q_A = latent heat + sensible heat, liquid - sensible heat, vapor + heat dilution
= 296 + 21.94 (52.4 - 47) 1.97 - 0.77 (47 - 6) + 38
= 536 kJ/kg ref. circulated.

Q_A/Q_E = 2.10 Q_G/Q_E = 2.39

Q_C/Q_E = 1.37 Q_{HX}/Q_E = 9.58

Q_{pump} = 105 watts (density ≈1,000 kg/m^3, eff = 50%, neglect ΔP across HX)

Heat exchanger log mean temperature difference 5.74°C.

4-1.2.2 Comments - System cis 1,2 dichloroethylene/M-12

This system looks far worse than did the R-21/tetraethylene glycol dimethyl ether primarily because the accurate vapor pressure data gives a more realistic picture of the small concentration difference with which we must cope and its consequences. While some of our data are fairly roughly approximated, the uncertainties are nowhere near great enough to improve the cycle to the point of interest.

Some improvements could be made in the cycle:

1. Increase the size of the heat exchanger. The heat exchanger used would be considered enormous by present absorption standards; to make this cycle at all interesting from a COP point of view, it would have to be several times larger since as the efficiency increases above 90%, already a very efficient heat exchanger, the log mean temperature difference decreases rapidly and the size of heat exchanger will vary inversely with the LMTD. Other problems would also be encountered, such as keeping up the velocity along the strong side surface with a head of only about 50 kPa available.

2. Choose closer approaches between the cooling air and the absorber and condenser. Again, we have the problem of proliferation of surface. In the absorber, we might have a problem with wetting the increased surface. In any case, to decrease the temperature approaches in these subsystems is probably possible but will require "smart" design. We will do some calculations below to see quantitatively what effects might result.

3. Exchange of sensible heat between hot condensate (stream 2) and cold vapor leaving the evaporator (stream 3) and between hot vapor from the generator (stream 1) and entering weak solution (stream 5) would also help the COP of the system, but with added surface. These could be direct contact heat exchangers, such as have been employed in absorption systems.

4-1.3.1 The System cis 1,2 dichloroethylene/M-6

The analysis of the system cis 1,2 dichloroethylene-N,N dimethylhexamide is interesting because, when compared to 4-1.2.1, it illustrates the effects of a change of absorbent molecular weight without altering refrigerant acidity or absorbent basicity. The raw laboratory data for the vapor pressures of this system are given in Table 5 and the constants of the corresponding Duhring equations are given in Table 6 , derived with the use of the vapor pressure equation for cis 1,2 dichloroethylene given in 4-1.2.1.

These constants were fitted to quadratic equations, i.e.,

$$m = 1.501 - 0.01288[x] + 0.000042 \ [x]^2$$

$$b = -216.3 + 5.488 \ [x] - 0.0403 \ [x]^2$$

which can be combined to give the equation:

$$T_{ref} = T_{sol} \ [1.501 - 0.01288 \ (x) + 4.2 \ \text{EE} \ (-5)(x)^2] - 216.3 + 5.488 \ (x) - 0.0403(x)^2$$

whose loci for different weight percent concentrations (x) of M-6 are shown in Figure 7.

TABLE 5

Vapor Pressures of cis 1, 2 Dichloroethylene/N,N Dimthylhexamide (M-6)
(Laboratory Data)

cis 1, 2 Dichloroethylene and M-6

85.67% M-6		97.48% M-6		95.66% M-6		76.69% M-6	
T (°C)	P (in Hg)	T (°C)	P (in Hg)	T (°C)	P (in Hg)	T (°C)	P (in Hg)
21.5	0.50	20.0	0.05	20.0	0.14	30.0	1.45
25.0	0.75	30.0	0.15	25.0	0.20	35.0	2.00
30.0	0.98	35.0	0.20	30.0	0.25	40.0	2.35
35.0	1.22	40.0	0.25	40.0	0.40	45.0	2.80
40.0	1.45	45.0	0.32	50.0	0.60	50.0	3.45
45.0	1.75	50.0	0.40	60.0	0.85	55.0	4.20
50.0	2.06	55.0	0.48	70.0	1.30	60.0	5.00
55.0	2.58	60.0	0.60	80.0	1.90	65.0	6.00
60.0	3.06	70.0	0.88	90.0	2.60	70.0	7.05
65.0	3.59	80.0	1.21	100.0	3.58	75.0	8.40
70.0	4.23	90.0	1.75	105.0	4.18	80.0	9.70
75.0	5.00	100.0	2.40	110.0	4.80	85.0	11.45
80.0	5.85	105.0	2.80	115.0	5.58	90.0	13.20
85.0	6.80	110.0	3.30	120.0	6.50	95.0	15.15
90.0	7.94	115.0	3.80	125.0	7.41	100.0	17.35
95.0	9.15	120.0	4.45	130.0	8.40	105.0	19.80
97.5	9.80	130.0	6.00			110.0	22.60
100.0	10.50	135.0	6.85			115.0	25.70
102.5	11.25	140.0	7.75			120.0	29.30
105.0	12.00						
110.0	13.75						
115.0	15.60						
120.0	17.68						
125.0	20.00						
130.0	22.60						
135.0	25.40						

TABLE 5 (cont'd.)

72.00% M-6		95.21% M-6		88.20% M-6		68.10% M-6	
T (°C)	P (in Hg)	T (°C)	P (in Hg)	T (°C)	P (in Hg)	T (°C)	P (in Hg)
20.5	1.18	20.0	0.20	20.0	0.40	20.0	1.40
25.0	1.48	25.0	0.20	30.0	0.60	25.0	1.65
30.0	1.80	30.0	0.25	40.0	0.95	30.0	2.05
35.0	2.25	40.0	0.45	45.0	1.20	35.0	2.65
40.0	2.80	45.0	0.55	50.0	1.45	40.0	3.35
45.0	3.45	50.0	0.64	55.0	1.75	45.0	4.15
50.0	4.20	60.0	1.00	60.0	2.15	50.0	5.04
55.0	5.15	70.0	1.40	65.0	2.55	53.0	5.70
60.0	6.15	80.0	1.98	70.0	3.00	61.5	7.80
65.0	7.35	90.0	2.80	75.0	3.60	65.0	8.70
70.0	8.70	100.0	3.85	80.0	4.35	70.0	10.30
75.0	10.40	110.0	5.10	85.0	5.20	75.0	12.15
80.0	12.05	120.0	6.80	90.0	5.95	80.0	14.35
85.0	14.00	130.0	9.00	95.0	6.85	85.0	16.60
90.0	16.20	140.0	11.65	100.0	7.85	90.0	19.10
95.0	18.62	150.0	14.95	105.0	9.00	95.0	21.85
100.0	21.30	160.0	18.80	110.0	10.30	100.0	24.95
105.0	24.40	170.0	23.90	115.0	12.00	105.0	28.50
110.0	27.75			120.0	13.65	106.5	29.40
112.5	29.60			125.0	15.60		
				130.0	17.60		
				140.0	22.10		
				150.0	27.80		
				153.5	29.80		

TABLE 5 (cont'd.)

cis Dichloroethylene in M-6

47.60 wt % M-6		80.15% M-6		82.87% M-6		91.52% M-6	
T (°C)	P (in Hg)	T (°C)	P (in Hg)	T (°C)	P (in Hg)	T (°C)	P (in Hg)
23.2	3.10	19.5	0.80	18.5	0.50	25.3	0.35
25.0	3.35	25.0	1.03	20.0	0.55	30.0	0.50
30.0	4.05	30.0	1.21	25.0	0.75	35.0	0.60
35.0	5.00	35.0	1.50	30.0	0.90	40.0	0.70
40.0	6.15	40.0	1.80	35.0	1.15	45.0	0.86
45.0	7.60	45.0	2.25	40.0	1.40	50.0	1.10
50.0	9.05	50.0	2.75	45.0	1.80	55.0	1.35
55.0	11.00	55.0	3.40	50.0	2.22	60.0	1.60
60.0	13.20	60.0	4.05	55.0	2.70	65.0	2.00
65.0	15.60	65.0	4.85	60.0	3.25	70.0	2.40
70.0	18.15	70.0	5.70	65.0	3.90	75.0	2.82
75.0	21.25	75.0	6.80	71.7	5.10	80.0	3.35
80.0	24.70	80.0	8.00	75.0	5.70	85.0	3.90
85.0	28.75	85.0	9.20	80.0	6.62	90.0	4.55
86.3	29.70	90.0	10.80	85.0	7.80	95.0	5.40
		95.0	12.40	90.0	9.00	100.0	6.25
		100.0	14.25	95.0	10.40	105.0	7.05
		105.0	16.50	100.0	12.00	110.0	8.20
		110.0	18.55	105.0	13.70	115.0	9.45
		115.0	21.05	110.0	15.70	120.0	10.80
		120.0	23.90	115.0	17.80	125.0	12.20
		125.0	27.00	120.0	20.20	130.0	13.90
		129.2	29.60	125.0	22.80	135.0	15.75
				130.0	25.90	137.5	16.75
				135.0	28.95		
				136.5	30.00		

TABLE 6

Duhring Constants for the System cis 1, 2 Dichloroethylene/M6 at Various Weight Percentages of M-6

$$Tref = mT_{sol} + b$$

[X] wt % M-6	m	b
85.67	.7047	-40.85
97.48	.6519	-67.72
95.66	.6562	-60.35
76.69	.7564	-33.09
72.00	.7906	-31.02
95.21	.6465	-58.17
88.20	.6896	-46.52
68.10	.8247	-29.08
47.60	.8776	-17.82
80.15	.7365	-36.59
82.87	.7436	-41.87
91.52	.6778	-50.77

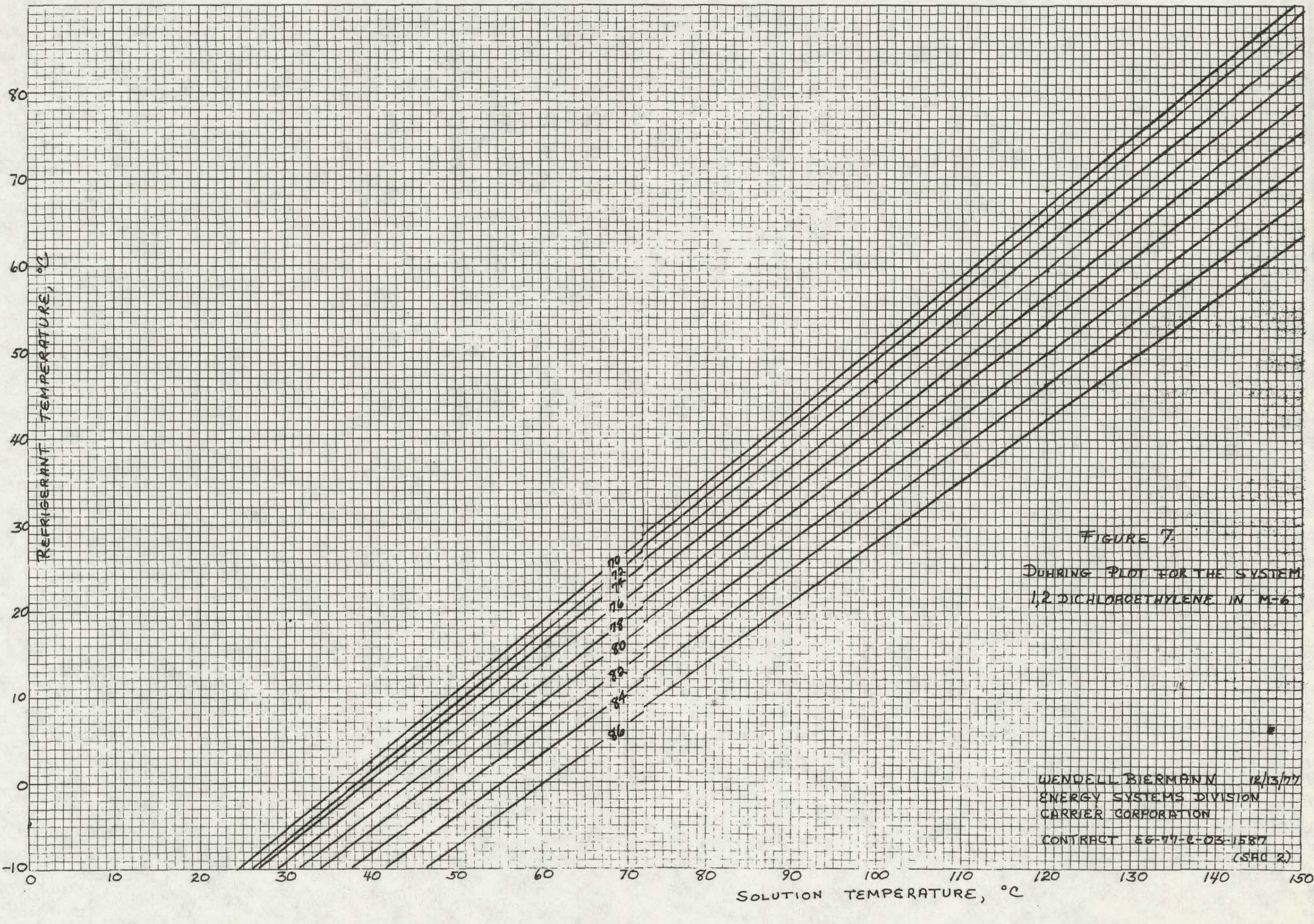


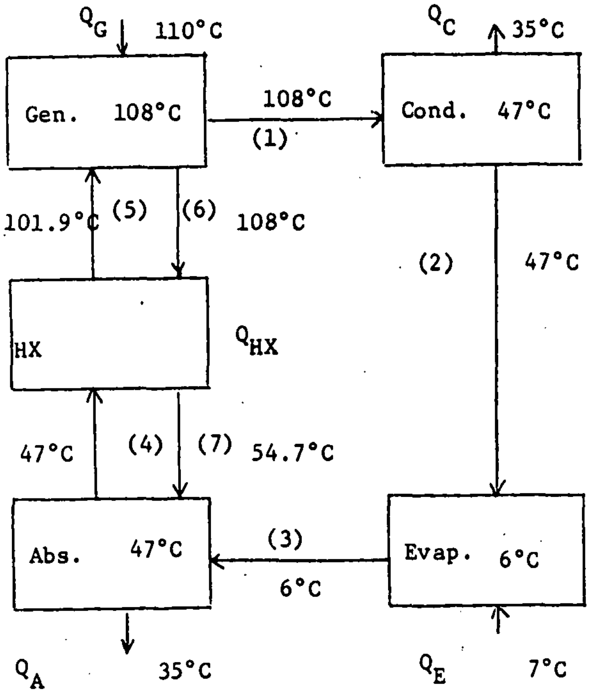
FIGURE 7.

DUHRING PLOT FOR THE SYSTEM 1,2 DICHLOROETHYLENE IN M-6

WENDELL BIERMANN 12/13/77
ENERGY SYSTEMS DIVISION
CARRIER CORPORATION

CONTRACT EG-77-C-03-1587
(SAC 2)

4-1.3.1 System 1,2 dichlorethylene - N,N dimethylhexamide (M-6) Air Cooled



1. Superheated Ref. Vapor
2. Liquid Refrigerant
3. Saturated Ref. Vapor
4. Weak Sol. to HX
5. Weak Sol. to Gen.
6. Strong Sol. to HX
7. Strong Sol. to Abs.

No rectifier needed. Neglect thermal effects of generator liquid bleed stream and condenser vapor purge stream.

Point	Temp. °C	[X] Wt % abs.	W kg/kg-ref.	h kJ/kg	Wh kJ/kg-ref	Pressure kPa	Dew Pt °C	Q kJ/kg-ref	Q'(Q_E=10kW 143 kg/hr ref
1	108	0	1			69.4	47	Q_E = 251	10 kW
2	47	0	1			69.4	47	Q_A = 534	21.3 kW
3	7	0	1			12.4	6	Q_G = 512	20.4 kW
4	47	73.6	16.02			12.4	6	Q_C = 343	13.7 kW
5		73.6	16.02			69.4	47	Q_{HX} = 1600	63.4 kW
6	108	78.5	15.02			69.4	47		
7		78.5	15.02			12.4	6	COP = 0.49	

$$x_2\ (73.6) = \frac{0.736/143}{0.736/143 + 0.264/97} = 0.65 \qquad x_2(78.5) = \frac{0.785/143}{0.785/143 + 0.215/97} = 0.71$$

Cp (73.6%) = 0.65 x 2.21 + 0.35 x 1.105 = 1.82 kJ/kg-°K

Cp (78.5%) = 0.71 x 2.21 + 0.39 x 1.105 = 2.00 kJ/kg-°K

Q_{max} weak stream = 1778 kJ/kg ref. circulated

Q_{max} strong stream = 1832 kJ/kg ref. circulated.

Assume HX is 90% efficient.

Q_{HX} = 0.90 x 1778 = 1600 kJ/kg ref. circulated.

$1600 = (108 - t_7) \times 2.00 \times 15.02$

$t_7 = 54.7$

$(t_5 - 47)/108 - 47 = 0.9$

$t_5 = 101.9$

ΔH vap = 296 kJ/kg at 59°C boiling point (see 4-1.2.1).

Cp (vapor) = 0.77 kJ/kg-°K

Q_C = 343 kJ/kg refrigerant (from 4-1.2.1)

Q_E = 251 kJ/kg refrigerant (from 4-1.2.1)

Q_G = sensible heat + latent heat + heat dilution

$= (108 - 101.9) \times 16.02 \times 1.82 + 296 + 38$

= 512 kJ/kg refrigerant

Q_A = latent heat + sensible heat, liquid - sensible heat, vapor + heat dilution

$= 296 + (54.7 - 47) \times 2.00 \times 15.02 - 0.77\ (47 - 6) + 38$

= 534 kJ/kg refrigerant

$Q_A/Q_E = 2.13$ $\qquad$ $Q_G/Q_E = 2.04$

$Q_C/Q_E = 1.37$ $\qquad$ $Q_{HX}/Q_E = 6.34$

Heat exchanger log mean temperature difference = 6.87 °C.

4-1.3.2 Comments, cis 1,2 dichloroethylene/M6

When we compare this to the previous M-12 system, we note that the lower absorbent molecular weight leads to a 36% increase in the concentration difference at otherwise equivalent conditions. This has no significant charge on the evaporator or condenser (we assume both absorbents are of low enough volatility that any rectification will not significantly affect our energy balances). The effect on the generator is a 15% decrease in loading, a 33% decrease in heat exchanger loading and a further assistance to the heat exchanger in that the same percentage efficiency can be achieved with a larger log mean temperature difference. Our approximations obscure the relief which should also be found with absorber loading.

It is also apparent that fan power and solution heat exchanger pump power will also benefit significantly from the decreased molecular weight of absorbent.

On an intuitive basis, it was felt that M-6 was about as low a molecular weight amide as should be used without postulating a rectifier. An attempt was made, however, to further lower the molecular weight without increasing volatility by using molecules with two disubstituted amide groups, as will be described below.

4-1.4.1 1,2 dichloro-1,2-difluoroethylene/M-6

The study of the system 1,2 dichloro-1,2-difluoroethylene in N,N dimethylhexamide (M-6) was useful since if a significant amount of absorbent-refrigerant interaction took place through electron donation to the π bond, the substitution of fluorine atoms for hydrogen should strongly improve interaction by withdrawing electron density from the C=C bond. On the other hand, if the predominate interaction is hydrogen bonding, this substitution should make 1,2-dichloro-1,2-difluoroethylene markedly inferior in interaction to the previously studied dichloroethylene.

The vapor pressure data taken in the laboratory are presented in Table 6. The material used was an approximately equimolar mixture of the cis and trans forms. This was combined with the refrigerant vapor pressure data, in Table 7 which could be represented by the empirical equation:

$$\ell nP = \frac{-3308.6}{T} + 15.951$$

where P is the vapor pressure in kiloPascals and T is the corresponding temperature in degrees Kelvin.

These two groups of information were combined as shown in Table 8 to give an equation whose loci are the Duhring plots at smoothed concentrations shown in Figure 8.

TABLE 6a

Vapor pressures of 1,2 dichloro-1,2-difluoroethylene in N,N-dimethylhexamide (M-6) Original Data

92.23%M-6		95.854%M-6	
T(°C)	P(in Hg)	T°C	P(in Hg)
23.3	3.30	21.1	1.62
25.7	3.60	26.7	2.39
27.5	3.78	27.5	2.43
30.0	4.03	30.0	2.70
35.0	4.80	35.0	3.12
40.0	5.62	41.7	3.91
45.0	6.44	45.0	4.23
55.0	8.58	50.0	4.88
60.0	9.74	55.0	5.53
65.2	11.12	60.0	6.30
67.5	11.80	65.1	7.21
70.0	12.44	70.0	8.31
75.0	13.98	75.0	9.18
80.0	15.40	80.0	10.21
85.0	17.13	90.0	12.69
90.0	19.02	95.0	14.00
95.0	21.19	100.0	15.32
100.0	23.03	105.0	16.90
105.0	25.30	110.9	18.70
110.5	27.90	115.0	20.20
115.2	29.03	120.0	22.03
		125.0	24.00
		130.0	26.21
		135.0	28.22

TABLE 6a(cont'd.)

79.29wt%M-6		63.36%M-6		93.68%M-6		86.63%M-6	
T°C	P(in Hg)	T(°C)	P(in Hg)	T(°C)	P(in Hg)	T(°C)	P(in Hg)
21.9	9.30	22.4	15.2	22.8	2.35	23.7	5.98
22.8	9.59	25.0	16.5	25.0	2.52	25.5	6.59
25.5	10.60	27.5	18.1	30.0	2.99	27.5	7.01
27.6	11.50	30.0	19.65	35.0	3.46	30.0	7.57
30.0	12.36	32.5	21.3	40.1	4.05	50.0	12.99
32.8	13.50	35.0	23.15	45.4	4.79	54.0	15.55
36.0	15.00	36.0	24.05	48.0	5.04	60.0	18.35
37.5	15.90	37.0	24.65	50.0	5.40	65.0	20.79
40.0	16.90	38.0	25.42	52.0	5.75	70.0	23.50
42.8	18.40	39.0	26.30	55.1	6.20	75.0	25.95
45.5	20.00	40.00	27.05	58.1	6.79	80.0	28.80
47.5	21.20	41.0	27.95	60.0	7.01	81.3	29.24
50.1	22.90	42.0	28.9	62.0	7.40		
53.0	24.50	43.0	29.96	65.0	8.00		
55.5	26.20			68.3	8.60		
58.0	27.95			72.3	9.60		
60.0	29.65			75.1	10.11		
				80.3	11.30		
				85.5	12.60		
				90.7	13.70		
				96.0	15.5		
				100.0	16.22		
				105.0	18.00		
				110.6	19.68		
				115.0	21.29		
				120.0	23.15		
				125.0	25.23		
				130.0	27.22		
				135.4	29.65		

TABLE 6a(cont'd.)

92.635wt % M-6		89.06 %M-6		41.20% M-6		91.05% M-6	
T(°C)	P(in Hg)	T°C	P(in Hg)	T(°C)	P(in Hg)	T(°C)	P(in Hg)
21.8	2.30	23.0	5.04	22.5	21.97	29.3	5.4
24.0	2.50	25.0	5.50	24.0	23.13	30.0	5.61
25.0	2.60	30.0	6.42	25.0	24.00	35.0	6.54
30.0	3.08	35.0	7.53	27.5	26.20	40.0	7.63
35.0	3.80	39.0	8.51	30.0	28.50	45.0	8.99
40.0	4.20	42.5	9.50	31.5	29.70	50.0	10.30
45.0	4.82	45.0	10.20			55.0	11.81
53.5	6.20	50.0	11.65	0 °	10.00	60.5	13.70
55.0	6.44	55.0	13.40	4.5°	11.93	65.0	15.34
60.0	7.24	60.0	15.22	7.0°	12.82	70.0	17.21
65.0	8.22	65.0	17.40	8.0°	13.51	77.5	20.81
70.0	9.20	70.7	19.54	10.0°	14.50	80.0	21.91
75.0	10.40	75.0	21.53	14.0	16.90	85.0	24.21
80.0	11.53	80.0	24.10	16.0	18.10	90.7	27.20
82.5	12.20	85.0	27.20	20.0	20.98	95.0	29.59
90.0	14.04	87.5	27.9	22.5	22.80		
95.0	15.48			25.0	24.84		
100.0	17.00						
105.0	18.60						
112.5	21.20						
115.0	22.02						
120.0	23.90						
126.0	26.20						
130.0	27.90						
133.7	29.30						

TABLE 7

Vapor Pressures of cis/trans 1,2 dichloro -1,2-difluoroethylene at various temperatures.

T(°C)	P(in Hg)
- 9.2	8.65
- 8.0	9.00
- 4.75	10.70
- 2.0	12.10
0.0	13.35
+ 2.0	14.95
4.0	16.26
6.0	17.80
8.0	19.70
10.0	21.30
12.0	23.00
14.0	25.15
16.0	27.15
18.0	28.80
19.0	29.90

TABLE 8

Constants for Duhring Equations for cis/trans 1,2 dichloro 1,2 difluoroethylene in M-6 at various weight percentages of M-6.

[x]	m	b
79.29	.6899	-22.89
63.36	.7623	-14.45
93.68	.4120	-37.25
86.63	.6011	-30.09
92.635	.4060	-35.84
89.06	.5449	-30.39
41.20	.8517	- 7.30
91.05	.5390	-32.54
92.23	.4622	-34.23
95.854	.4240	-39.92

$$m = 2.1910 + .08578\,x - .000618x^2$$

$$b = 61.07 - 1.730x + 0.0158x^2$$

$$T_{ref} = (-2.191 + .08578\,x - .000618x^2)\,T_{sol}$$

$$+ (61.07) - 1.730x + 0.0158x^2$$

Equation valid 60 - 95 not % absorbent

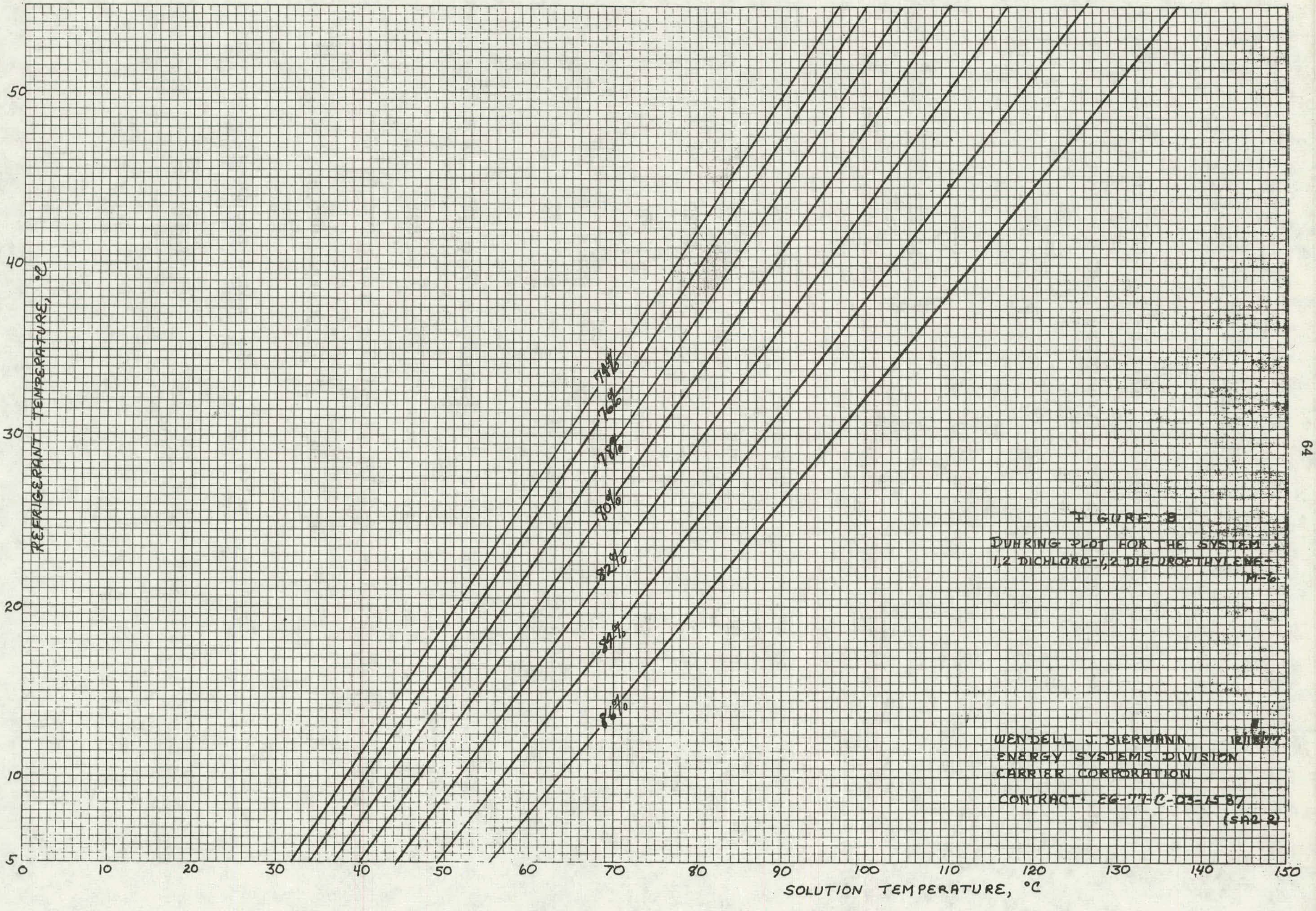


FIGURE 8

DUHRING PLOT FOR THE SYSTEM
1,2 DICHLORO-1,2 DIFLUROETHYLENE-
M-6

WENDELL J. BIERMANN 12/18/77
ENERGY SYSTEMS DIVISION
CARRIER CORPORATION

CONTRACT: EG-77-C-03-1587
(SA2 2)

4-1.4.2 Comments, 1,2 dichloro-1,2-difluoroethylene/M-6

From the Duhring curves, using the same conditions as have previously been adopted for comparison purposes, the high and low side concentrations can be seen to be 82.8 and 82.5 weight percent, respectively. Additional cycle calculations are evidently superfluous since the solution flow would be enormous.

It is evident from this system, as well as observations made elsewhere in this report, that effective halocarbon absorption requires the presence of a hydrogen atom on the refrigerant molecule.

4-1.5.1 Trichloroethylene-N,N dimethyldodecamide (M-12)

The poor performance of tetrahalogenated ethylene suggested that a trihalogenated ethylene, in which the single hydrogen would have its basicity promoted by three halogen atoms, should be more promising than the previously considered systems. Trichloroethylene being readily available, non-flammable, stable, etc., appeared to be a candidate.

Vapor pressures of trichloroethylene are shown in Table 9, vapor pressures of trichloroethylene/M-12 solutions in Table 10 and the constants for the Duhring equations derived from the data in Tables 9 and 10 are tabulated in Table 11.

These data are combined in the equation:

$$T_{ref} = [1.0966 - 0.0034\ (x)]\ T_{sol} + 7.83 - 0.431\ (x)$$

where (x) is the concentration of M-12 on a weight percent, T_{ref} and T_{sol} are the isobaric refrigerant and solution temperatures, respectively. The loci of this equation are the Duhring plots of Figure 9.

4-1.5.2 Evaluation of Trichloroethylene/M-12

The Duhring plot, if taken literally, would suggest that the concentration spread between weak and strong solutions, under the air cooled conditions adopted as standard in the previously studied systems, would be between 88% M-12 and about 97%. Unfortunately, the available data were lacking in high concentration results and treatment of the system would have to be done on the basis of a blind extrapolation, which is far too risky. Additional data should be taken.

The system is not particularly promising:

1. The low solubility means that the circulation rate will be higher than would be experienced for a more soluble material showing a similar concentration spread.

2. The high molecular weight means that the ratio of latent heat to heat capacity, on a unit mass basis, will be low.

TABLE 9

VAPOR PRESSURES, TRICHLOROETHYLENE

T °C	P (in Hg)	T °C	P (in Hg)	T °C	P (in Hg)
23	3.06	47.5	9.48	70.0	20.48
25	3.40	50.0	10.41	72.5	22.15
30	4.25	52.5	11.39	75.0	23.92
35	5.60	55.0	12.37	77.5	25.82
37.5	6.42	57.5	13.49	80.0	27.61
40.0	7.15	60.0	14.60	81.0	28.85
42.8	7.90	62.5	16.21	82.2	29.80
45.5	8.80	65.0	17.38	82.5	30.20
		67.5	18.80		

$$\ell n P = \frac{-3947.8}{T} + 15.77$$

where P is the pressure in kiloPascals and T the absolute temperature in degrees Kelvin.

TABLE 10

VAPOR PRESSURES, TRICHLOROETHYLENE IN M-12

44.09 wt% M-12		61.54 wt% M-12		77.17 wt% M-12		70.35 wt% M-12	
°C	P (in Hg)	°C	P (in Hg)	°C	P (in Hg)	°C	P (in Hg)
21.1	1.45	21.0	1.00	25.0	0.70	27.5	1.18
25.0	2.00	25	1.25	30.0	0.90	30.0	1.32
30	2.53	30	1.60	35.0	1.14	35.0	1.68
35	3.20	35	2.00	40	1.38	40.0	2.15
40	4.00	40	2.55	45	1.74	45.0	2.61
45	4.92	45	3.21	50	2.21	50.0	3.28
50	6.02	50	3.95	55	2.72	55.0	4.00
55	7.38	55	4.81	60	3.27	60.0	4.80
60	8.98	60	5.95	65	3.98	65.0	5.90
65	10.76	65	7.03	70	4.77	70.0	6.95
67.5	11.70	70	8.45	75	5.74	75.0	8.40
70.0	12.80	75	10.19	80	6.75	80.0	9.80
72.5	13.95	80	11.94	85	7.94	85.0	11.60
75.0	15.10	85	13.95	90	9.25	88.0	12.87
77.7	16.42	90	16.40	95	10.82	90.5	14.06
80.3	17.60	92.5	17.72	100	12.54	92.5	14.61
82.9	19.17	95	19.02	105	14.00	95.0	15.86
85.5	21.00	97.5	20.40	115	18.05	97.5	17.10
88.1	22.53	100	21.60	120	20.45	100	17.83
90.7	24.50	102.5	22.67	125	23.20	102.5	19.35
93.3	25.90	105	24.22	127.5	24.52	105	20.45
95.9	27.80	107.5	25.90	130.0	25.86	107.5	22.04
98.5	29.60	110	27.50	132.5	27.41	110	23.38
		112.5	29.55	135.0	29.00	112.5	25.30
				136.2	29.60	115.0	26.30
						117.5	28.32
						120.0	29.72

TABLE 10 (cont'd.)

83.74 wt% M-12		28.2 wt% M-12		51.91 wt% M-12	
°C	P (in Hg)	°C	P (in Hg)	°C	P (in Hg)
30	0.75	20	1.98	22	1.40
35	0.96	22.5	2.35	25	1.64
40	1.27	25.0	2.62	30	2.06
45	1.50	30.0	3.22	35	2.70
50	1.82	35.0	4.13	40	3.34
55	2.25	40.0	5.02	45	4.19
60	2.80	45.0	6.34	50	5.02
65	3.38	47.5	6.98	55	6.18
70	4.05	50.0	7.66	60	7.45
75	4.95	52.5	8.39	65	9.20
80	5.85	55.0	9.26	70	10.78
85	6.97	57.5	10.25	75.1	12.95
90	8.07	60.0	11.20	77.7	14.03
95	9.60	62.5	12.23	80.3	15.20
100	11.02	65.0	13.38	82.9	16.44
105	12.36	67.5	14.70	85.5	17.69
110	14.20	70.0	15.80	88.1	19.23
115	16.50	72.5	17.33	90.7	20.69
120	18.40	75.1	19.02	93.3	22.27
125	21.00	77.7	20.20	95.9	23.92
130	23.40	80.3	21.78	98.5	25.74
		82.9	23.68	101	27.20
		85.5	25.45	103.5	29.10
		88.1	27.56	104.0	29.60
		90.7	29.58		

TABLE 11

CONSTANTS FOR THE DUHRING EQUATIONS, TRICHLOROETHYLENE/M-12

$$T_{ref} = m\, T_{sol} + b$$

(x) Wt % M-12	m	b
83.74	0.8087	-29.35
28.20	0.9747	-6.08
51.91	0.9261	-13.81
49.09	0.9573	-11.31
61.54	0.9001	-18.44
77.17	0.7979	-25.58
70.35	0.8770	-22.13

$m = 1.0966 - 0.0034\ (x)$

$b = 7.83 - 0.431\ (x)$

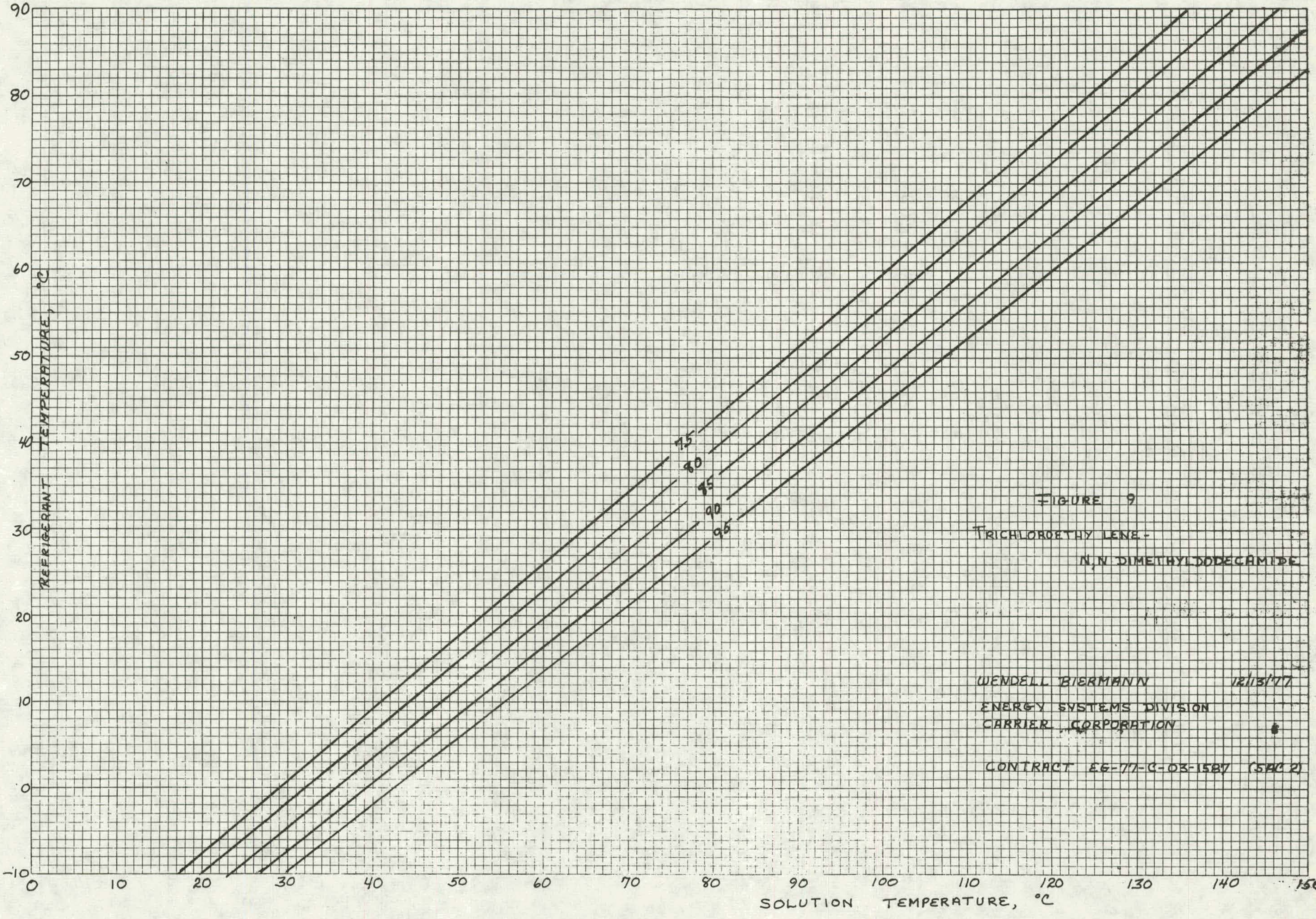


FIGURE 9

TRICHLOROETHY LENE-
N,N DIMETHYLDODECAMIDE

WENDELL BIERMANN 12/13/77
ENERGY SYSTEMS DIVISION
CARRIER CORPORATION

CONTRACT EG-77-C-03-1587 (SAC 2)

4-1.5.3 Fluorodichloromethane (R-21) with N,N Dimethylhexamide (M-6)

This refrigerant appears to be an excellent choice for an absorption system of the "organic" type since it has a low molecular weight, one hydrogen atom and three highly electronegative halide atoms to enhance the acidity of the hydrogen atom. It is also a stable refrigerant and has a boiling point (about 9°C) which would permit low pressure operation.

Table 12 displays the constants which relate the temperature of a series of solutions of R-21 in M-6 to the isobaric temperature of R-21. Vapor pressure data for R-21 were daken from Table 6, ASHRAE Handbook of Fundamentals (1972), as were the other properties of this refrigerant needed in cycle calculations.

The family of Duhring plots for R-21/M-6 are given in Figure 10.

A series of cycle calculations follow which project the principal characteristics of cycles operating with the system R-21/M-6:

1. Under "typical" air cooled, solar powered conditions adopted earlier with a 70% efficient heat exchanger.

2. Under "typical" conditions as above, but with a 90% efficient heat exchanger.

3. Under "typical" conditions as above, but with a hypothetical 100% efficient liquid heat exchanger and a 100% effective liquid-suction heat exchanger across the evaporator.

4. With air side approach reduced from 12°C to 8°C and with a 90% efficient solution heat exchanger.

TABLE 12

CONSTANTS FOR DUHRING PLOTS, R-21/M-6

(X) Wt % M-6	m	b
88.81	0.5324	-59.45
85.01	0.5219	-47.66
75.05	0.5384	-42.30
67.89	0.7063	-41.00
65.99	0.7137	-38.90
64.43	0.7263	-36.70
55.64	0.7808	-30.80

$T_{ref} = m\, T_{sol} + b$, where T is in degrees Celsius.

$$T_{ref} = [1.2725 - 0.00873\,(x)]\, T_{sol} + 10.21 - 0.7322\,(x).$$

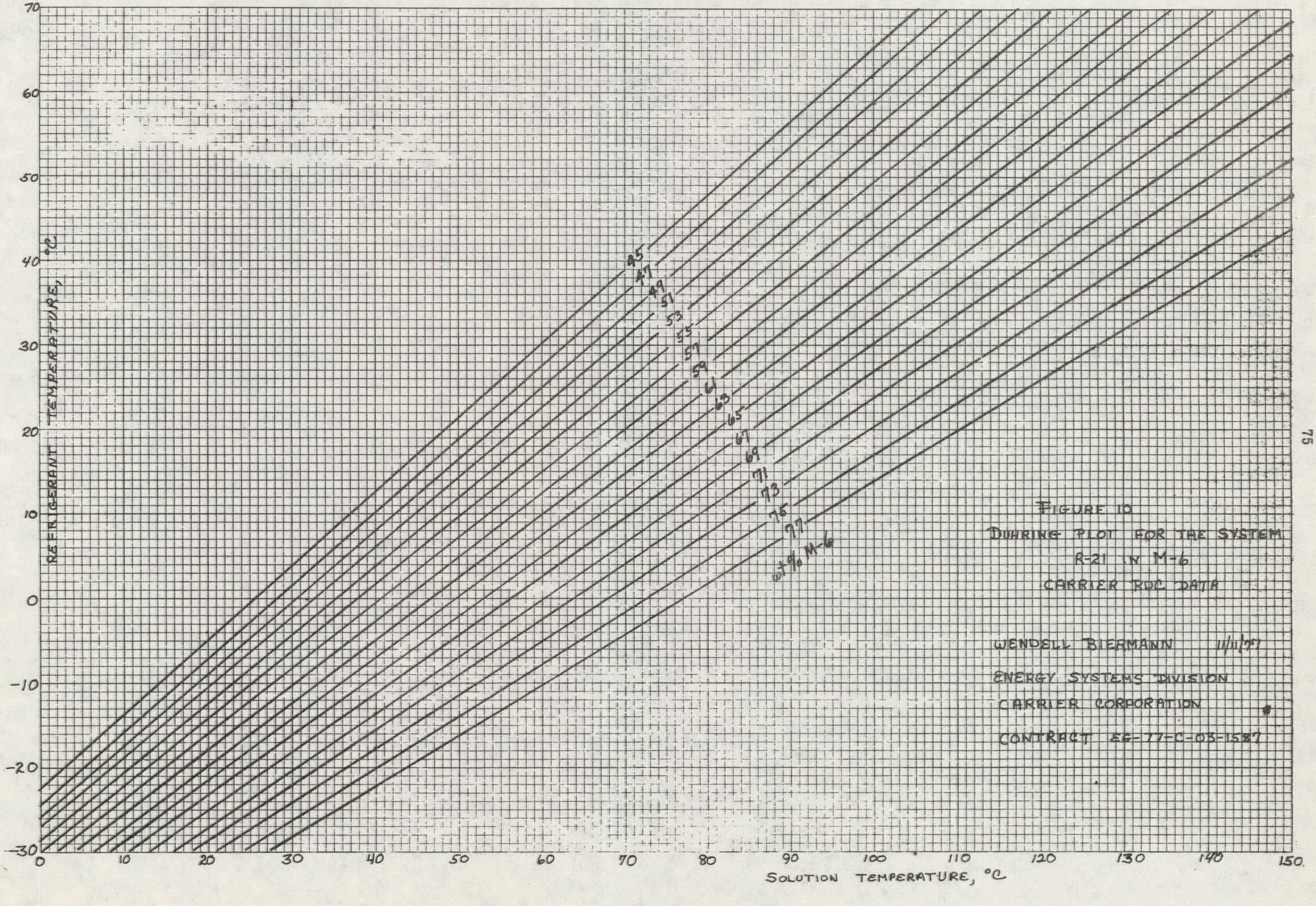


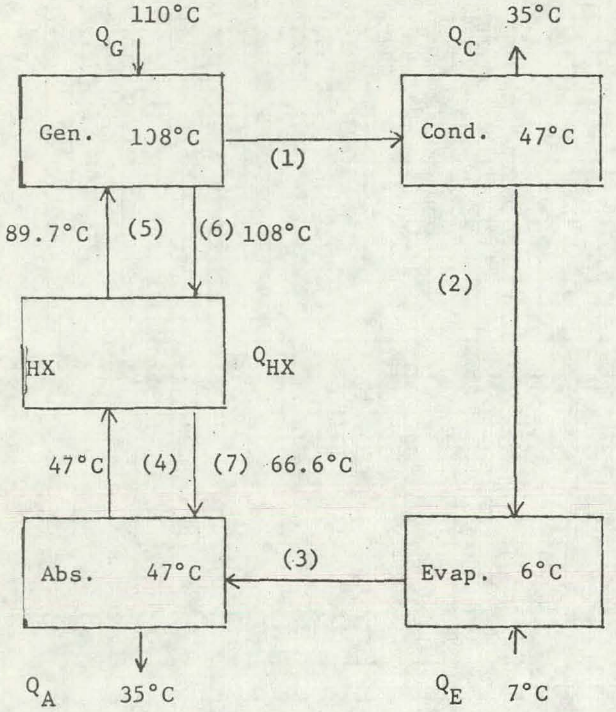
FIGURE 10
DUHRING PLOT FOR THE SYSTEM
R-21 IN M-6
CARRIER RDC DATA

WENDELL BIERMANN 11/11/77

ENERGY SYSTEMS DIVISION
CARRIER CORPORATION

CONTRACT EG-77-C-03-1587

System: Dichlorofluoromethane (R-21)/N,N Dimethylhexamide (M-6)   Air Cooled
HX = 70% eff.



1. Superheated Ref. Vapor
2. Liquid Refrigerant
3. Saturated Ref. Vapor
4. Weak Sol. to HX
5. Weak Sol. to Gen.
6. Strong Sol. to HX
7. Strong Sol. to Abs.

No rectifier needed. Neglect thermal effects of generator liquid bleed stream and condenser vapor purge stream.

Point	Temp. °C	[X] Wt % abs.	W kg/kg-ref.	h kJ/kg	Wh kJ/kg-ref	Pressure kPa	Dew Pt °C	Q kJ/kg-ref	Q'(Q_E=10kW 184 kg/hr ref
1	108	0	1	355	355	364	47	Q_E = 196	10 kW
2	47	0	1	90	90	364	47	Q_C = 265	13.5
3	6	0	1	286	286	91	6	Q_A = 698	35.6
4	47	56.0	14.65			91	6	Q_G = 635	32.4
5	86.8	56.0	14.65			364	47	Q_{HX} = 988	50.4
6	108	60.1	13.65			364	47		
7	65.3	60.1	13.65			91	6	COP=0.31	

$$\chi_2\ (56\%) = \frac{0.56/143}{0.56/143 + 0.46/103} = 0.47 \qquad \chi_2(60\%) = \frac{0.601/143}{0.601/143 + 0.399/103} = 0.52$$

C_p (R-21, 50°C) = 1.08 kJ/kg-°K C_p (R-21, 100°C) = 1.17 kJ/kg-°K

C_p (M-6) = 2.1 + (3 t x 10^{-3}) kJ/kg-°K $\Delta H_{diff} \approx$ 35 kJ/kg-refrigerant.

C_p (56%, 75°C) = 0.47 (2.1 + 3 x 75 x 10^{-3}) + 0.53 x 1.12
= 1.58 kJ/kg-°K

C_p (60%, 75°C) = 0.52 (2.1 + 3 x 75 x 10^{-3}) + 0.48 x 1.12
= 1.75 kJ/kg-°K

Q_E = 286 - 90 = 196 kJ/kg refrigerant circulated
Q_C = 355 - 90 = 265 kJ/kg ref. cir.

Q (strong stream) = 13.65 x (108 - 47) x 1.75 = 1457 kJ/kg ref.
Q (weak stream = 14.65 x (108 - 47) x 1.58 = 1412 kJ/kg ref.
Q_{HX} = 988

t_5 = 47 + 0.70 (108 - 47) = 89.7°C
988 = (108 - t_7) x 1.75 x 13.65
t_7 = 66.6°C

$Q_A = (h_{\ell,470} - h_{\nu,6°}) + \Delta H_d$ + 13.65 x 1.75 x (66.6 - 47)
= (286 - 90) + 35 + 468
= 698 kJ/kg ref. circulated.

$Q_G = (h_{\nu,108} - h_{\ell,108}) + \Delta H_D$ + 1.52 x 14.65 x (108 - 89.7)
= (355 - 162) + 35 + 408
= 635 kJ/kg ref. circulated.

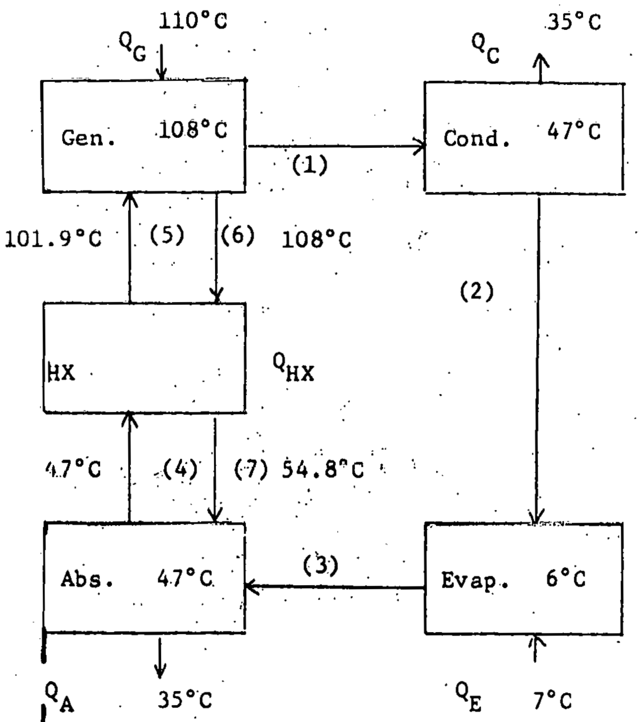
Q_C/Q_E = 1.35 Q_G/Q_E = 3.24

Q_A/Q_E = 3.56 Q_{HX}/Q_E = 5.04

Heat Exchanger LMTD = 18.9°C

System R-21/M-6

Air Cooled
HX = 90% Eff.



1. Superheated Ref. Vapor
2. Liquid Refrigerant
3. Saturated Ref. Vapor
4. Weak Sol. to HX
5. Weak Sol. to Gen.
6. Strong Sol. to HX
7. Strong Sol. to Abs.

No rectifier needed. Neglect thermal effects of generator liquid bleed stream and condenser vapor purge stream.

Point	Temp. °C	[X] Wt % abs.	W kg/kg-ref.	h kJ/kg	Wh kJ/kg-ref	Pressure kPa	Dew Pt °C	Q kJ/kg-ref	Q'(Q_E=10kW 184kg/hr ref
1	108	0	1	355	355	364	47	Q_E = 196	10.0 kW
2	47	0	1	90	90	364	47	Q_A = 417	21.3
3	7	0	1	286	286	91	6	Q_G = 369	18.8
4	47	56.0	14.65			91	6	Q_C = 265	13.5
5	101.9	56.0	14.65			364	47	Q_{HX} = 1271	64.8
6	108	60.1	13.65			364	47		
7		60.1	13.65			91	6	COP=0.53	

From Previous Calculation: C_p (56%, 75°C) = 1.58 kJ/kg-°K
C_p (60%, 75°C) = 1.75 kJ/kg-°K
Q_E = 196 kJ/kg ref. circulated
Q_C = 265 kJ/kg ref. circulated
Q_{max} (HX) = 1412 kJ/kg ref. circulated.

$t_5 = 47 + 0.90\ (108 - 47)$
$\quad = 101.9°C$

$Q_{HX} = 1412 \times 0.90 = (108 - t_7) \times 1.75 \times 13.65 = 1271$

$t_7 = 54.8°C$

$Q_A = (h_{\ell,470} - h_{\nu 6°}) + \Delta H_d + 13.65 \times 1.75 \times (54.8 - 47)$
$\quad = (286 - 90) + 35 + 186$
$\quad = 417$ kJ/kg ref. circulated.

$Q_G = (h_{\nu,\ 108} - h_{\ell,\ 108}) + \Delta H_D + 14.65 \times 1.58 \times (108 - 101.9)$
$\quad = (355 - 162) + 35 + 141$
$\quad = 369$ kJ/kg-ref. circulated.

$Q_C/Q_E = 1.35$ $\qquad$ $Q_G/Q_E = 1.88$

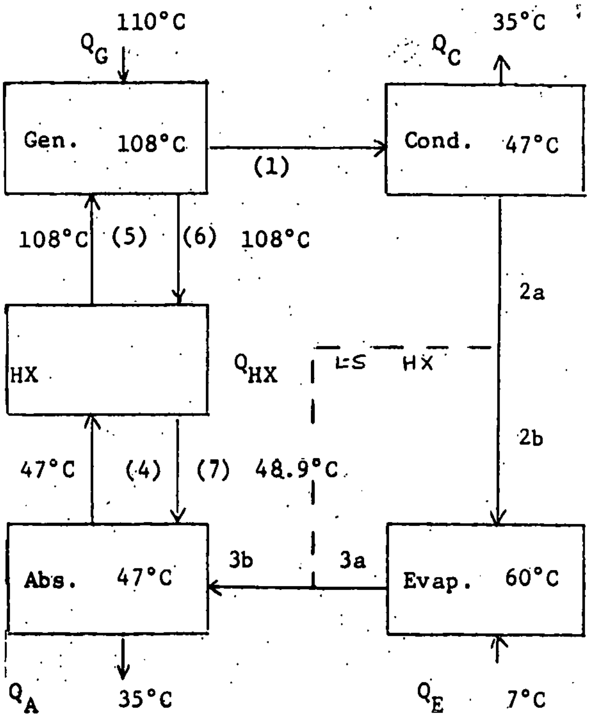
$Q_A/Q_E = 2.13$ $\qquad$ $Q_{HX}/Q_E = 6.48$

Heat Exchanger LMDT = 6.91°C

System M-6 and R-21

100% Efficient Solution HX

100% Efficient Liquid-Suction HX



1. Superheated Ref. Vapor
2. Liquid Refrigerant
3. Saturated Ref. Vapor
4. Weak Sol. to HX
5. Weak Sol. to Gen.
6. Strong Sol. to HX
7. Strong Sol. to Abs.

No rectifier needed. Neglect thermal effects of generator liquid bleed stream and condenser vapor purge stream.

Point	Temp. °C	[X] Wt % abs.	W kg/kg-ref.	h kJ/kg	Wh kJ/kg-ref	Pressure kPa	Dew Pt °C	Q kJ/kg-ref	Q'(Q_E=10kW 168kg/hr ref
1	108	0	1	355	355	1559	47	Q_C = 265	12.4 kW
2a	47	0	1	90.4	90.4	1559	47	Q_E = 214	10
2b		0	1	72	72	1559	47	Q_A = 249	11.6
3a	6°	0	1	286	286	364	6	Q_G = 275	12.9
3b		0	1	304	304	364	6	Q_{HX} = 1412	66.0
4	47	56.0	14.65			364	6		
5	106	56.0	14.65			1559	47		
6	108	60.1	13.65			1559	47	COP = 78%	
7	48.9	60.1	13.65			364	6		

L-S HX h(ℓ, 47°) = 90.4 kJ/kg　　h (ℓ, 6°) = 46.0 kJ/kg
h(v , 6°) = 286 kJ/kg　　h (v , 47°) = 304 kJ/kg

L-S $HX_{(max)}$ = 18 kJ/kg. Assume total exchange.

Stream (1) 355 kJ/kg　　h(v , sat 108°) 327 kJ/kg　　(28 kJ/kg superheat available)

Q_{HX} = 14.65 x 1.58 x (108 - 47) = 1412 kJ/kg refrigerant

1412 = 13.65 x 1.75 x (108 - t_7)

t_7 = 48.9°C

Q_A = (304 - 90) + 35 + (48.9 - 47) x 13.65 x 1.75
= 294 kJ/kg ref. circulated.

Q_G = (355 - 162) + 35
= 228 kJ/kg ref. circulated.

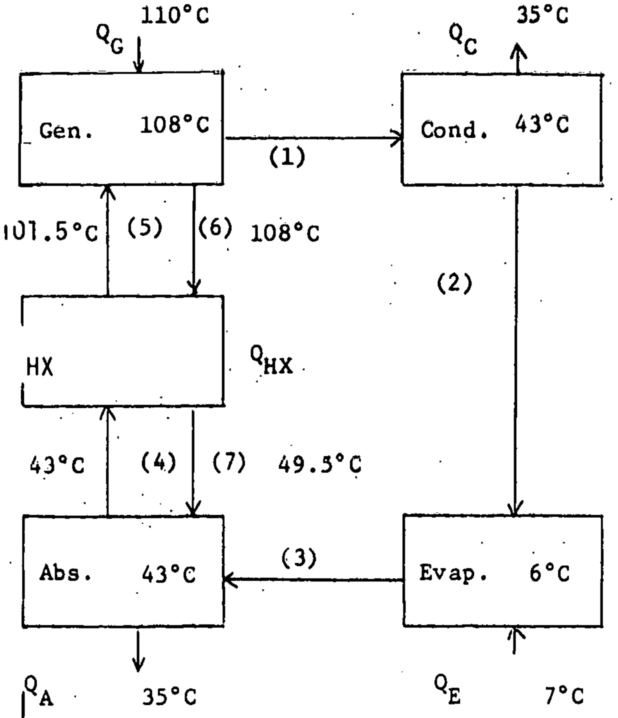
Q_C/Q_E = 1.24

Q_A/Q_E = 1.16

Q_G/Q_E = 1.29

Q_{HX}/Q_E = 6.60

System M-6/R-21 90% Heat Exchanger, 8°C Airside Approach



1. Superheated Ref. Vapor
2. Liquid Refrigerant
3. Saturated Ref. Vapor
4. Weak Sol. to HX
5. Weak Sol. to Gen.
6. Strong Sol. to HX
7. Strong Sol. to Abs.

No rectifier needed. Neglect thermal effects of generator liquid bleed stream and condenser vapor purge stream.

Point	Temp. °C	[X] Wt % abs.	W kg/kg-ref.	h kJ/kg	Wh kJ/kg-ref	Pressure kPa	Dew Pt °C	Q kJ/kg-ref	Q'(Q_E=10kW 180 kg/hr ref
1	108	0	1	350	350	321	43	Q_E = 200	10.0 kW
2	43	0	1	86	86	321	43	Q_C = 264	13.2
3	6	0	1	286	286	91	6	Q_A = 271	13.6
4	43	53.2	6.72			91	6	Q_G = 295	14.8
5	101.5	53.2	6.72			321	43	Q_{HX} =596	29.8
6	108	62.5	5.72			321	43		
7	49.5	62.5	5.72			91	6	COP=0.68	

$$x_2\ (53.2\%) = \frac{0.532/143}{0.532/143 + 0.468/103} = 0.45 \qquad x_2\ (62.5\%) = \frac{0.625/143}{0.625/143 + 0.375/103} = 0.55$$

C_p (R-21, 50°C) = 1.08 kJ/kg-°K C_p (R-21, 100°C) = 1.17 kJ/kg-°K

C_p (M-6) = $2.1 + (3t \times 10^{-3})$ kJ/kg-°K ΔH_{diff} = 35 kJ/kg-°K

C_p (53%, 75°C) = $0.45\ [2.1 + 3t \times 10^{-3}] + 0.55 \times 1.12 = 1.55$ kJ/kg-°K

C_p (62%, 75°C) = $0.55\ [2.1 + 3t \times 10^{-3}] + 0.45 \times 1.12 = 1.78$ kJ/kg-°K

$Q_E = 286 - 86 = 200$ kJ/kg refrigerant circulated
$Q_C = 350 - 86 = 264$ kJ/kg ref. circ.

Q(strong stream) $= 5.72 \times 1.78\ (108 - 43) = 662$ kJ/kg ref.
Q(weak stream) $= 6.72 \times 1.55\ (108 - 43) = 677$ kJ/kg ref.

$Q_{HX} = 0.90 \times 662 = 596$ kJ/kg ref.
$t_5 = 0.90\ (108 - 43) + 43 = 101.5$
$596 = (108 - t_7) \times 1.78 \times 5.72$
$t_7 = 49.5°\text{C}$

$$Q_G = h_\upsilon (108°) - h_\ell (108) + 6.72 \times 1.55 \times (108 - 101.5) + 35$$
$$= (350 - 158) + 68$$
$$= 295 \text{ kJ/kg ref.}$$

$$Q_A = [h_\upsilon\ (60) - h_\ell (43°)] + \Delta H_{dil} + (49.5 - 43) \times 5.72 \times 1.78$$
$$= [286 - 86] + 35 + 37$$
$$= 271$$

$Q_A/Q_E = 1.36$ $Q_G/Q_E = 1.48$

$Q_C/Q_E = 1.32$ $Q_{HX}/Q_E = 2.98$

Heat Exchanger LMTD = 6.5°C

4-1.5.8 Comments R-21/M-6 System

The several conditions under which cycle parameters were calculated give some feel for the design problems which must be faced in building a useful air cooled, solar driven, absorption chiller based on an "organic" cycle.

It is evident in comparing these results that one must have a very efficient solution heat exchanger if any useful efficiency is to be obtained and that it will be very large since the heat exchanger load is about six and a half times the size of the cooling load. The absorber and generator loads also tend to climb very fast as the heat exchanger drops in efficiency.

Under the standard design conditions, including a 12°C approach to the ambient air, the cycle efficiency is projected as 53%, with 78% estimated as a sort of theoretical ceiling if all possible heat conservation takes place. The liquid-suction heat exchange can potentially increase the evaporator performance by about ten percent, which cuts down the solution circulation rate by a similar amount.

Another way of improving the performance of the cycle is by reducing the approach temperature of the absorber and condenser to the cooling air. The number 8°C instead of 12° previously postulated is arbitrary. The effects of this are dramatic since it allows an increased concentration spread and a major decrease in solution circulation rate.

4-1.6.1 Difluorochloromethane (R-22)/N, N Dimethylhexamide (M-6)

The R-22/M-6 data were derived by measuring the vapor pressures of a series of solutions at various temperatures and converting the data to Duhring plots by use of refrigerant data published by E. I. duPont de Nemours and Co. (1964). Table 13 gives the values of the constants "m" and "b" derived by least squares fitting of the data to a linear curve.

A second least squaring of these constants gives a combined equation:

$$T_{ref} = [1.182 - 0.00758\ (x)]\ T_{sol} + 15 - 0.8722\ (x),$$

whose loci at rounded values of the weight percentage of M-6, (x), are shown in Figure 11.

TABLE 13

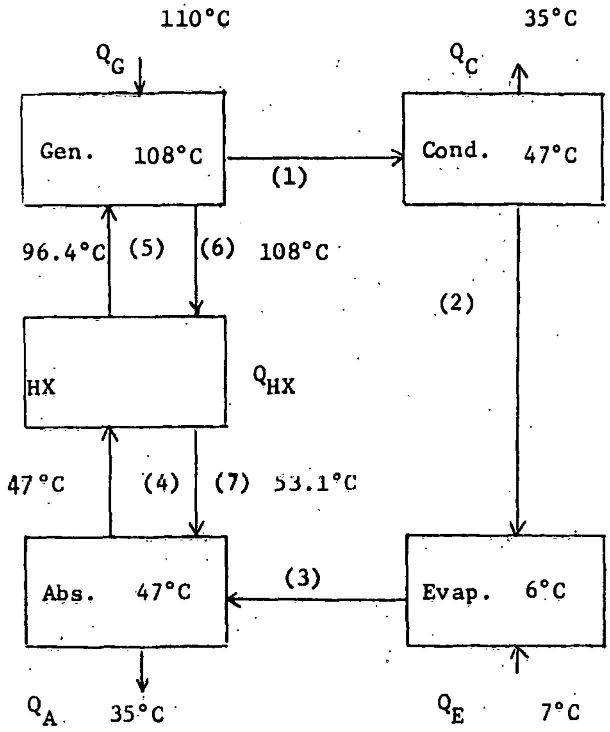
DUHRING EQUATION CONSTANTS FOR R-22/M-6

% wt M-6	m	b
90.62	0.4950	-64.79
87.98	0.4962	-59.60
84.30	0.5032	-55.50
82.03	0.5458	-55.25
76.40	0.6400	-52.64
75.30	0.6444	-51.34
71.43	0.6901	-47.79
62.50	0.7249	-38.72
57.05	0.7203	-34.72
55.15	0.7379	-30.

$T_{ref} = m\ T_{sol,\ x\%} + b$

System 4-1.6.1a Difluorochloromethane (R-22)/Dimethylhexamide (M-6)

Air Cooled Conditions



1. Superheated Ref. Vapor
2. Liquid Refrigerant
3. Saturated Ref. Vapor
4. Weak Sol. to HX
5. Weak Sol. to Gen.
6. Strong Sol. to HX
7. Strong Sol. to Abs.

No rectifier needed. Neglect thermal effects of generator liquid bleed stream and condenser vapor purge stream.

Point	Temp. °C	[X] Wt % abs.	W kg/kg-ref.	h kJ/kg	Wh kJ/kg-ref	Pressure kPa	Dew Pt °C	Q kJ/kg-ref	Q'(Q_E=10kW 243kg/hr ref
1	108	0	1	334		1812	47	Q_E= 148	10 kW
2	47	0	1	103.5		1812	47	Q_C= 230.5	15.6
3	7	0	1	251.5		603	6	Q_A= 413	27.9
4	47	52.7	14.18			603	6	Q_G= 496	33.5
5	101.9		14.18			1812	47	Q_{HX}= 1722	116.4
6	108	56.7	13.18			1812	47		
7			13.18			603	6	COP=30%	

$$\chi_2\ (56.7\%) = \frac{0.567/143}{0.567/143 + 0.433/87} = 0.443 \qquad \chi_2\ (52.7\%) = \frac{0.527/143}{0.527/143 + 0.473/87} = 0.404$$

C_p (M-6) = $2.1 + 4t \times 10^{-3}$ kJ/kg°K (0 - 100°C)

C_p (R-22) = $1.278 - 0.0169t + 0.00040t^2$ kJ/kg°K (6 - 100°C)

C_p (56.7%, 77°C) = $(1 - 0.443) \times 2.35 + 0.443 \times 2.41 = 2.38$ kJ/kg-°K.

C_p (52.7%, 77°C) = (1 - 0.404) x 2.35 + 0.404 x 2.41 = 2.46 kJ/kg-°K

Q (56.7%) =(108 - 47) x 13.18 x 2.38 = 1913 kJ/kg ref. circulated.

with 90% efficient heat exchanger:

Q_{HX} = 1722 kJ/kg ref. cir.

t_7 = 108 - 0.90 (108 - 47)

t_7 = 53.1 °C

1722 = 14.18 x 2.46 x (t_5 - 47)

t_5 = 96.4°C

Q_A = (254 - 103.5) + 35 + (56.7 - 47) x 13.18 x C_p (56.7, 50°C)

= 150.5 + 35 + 127.8 x (0.596 x 1.43 + 0.404 x 2.3)

= 413 kJ/kg solution circulated.

Since $Q_A + Q_C = Q_E + Q_G$

$Q_G = Q_C + Q_A - Q_E$ = 496 kJ/kg ref. circulated.

A direct calculation of Q_G is difficult since the critical temperature of R-22 is 96.0°C. In lieu of any knowledge of solution properties, we can assume that the apparent molar enthalpy of R-22 in solution will be equal to the molar enthalpy of pure R-22 at the same vapor pressure. If we do this:

$Q_G = h_v$ (108°C) - h_ℓ (47°C) + Cp (52.7%, 100°C) x 14.18 x (108 - 96.4)

= (362 - 108) + 404

= 658 kJ/kg ref. circulated.

In terms of the uncertainties involved, the value 496 is preferred.

Q_C/Q_E = 1.56

Q_G/Q_E = 3.35

Q_A/Q_E = 2.79

Q_{HX}/Q_E = 11.64

4-1.6.2 Comments - M-6/R-22

R-22 is a much higher pressure refrigerant than we have previously considered. This has two consequences; the molar heat of vaporization is lower (Trouton's Law) and the low critical temperature causes the specific heat of the refrigerant to increase rapidly through the temperature range. These two effects lead to a low Q_E value per unit mass of refrigerant circulated. A liquid-suction heat exchanger across the evaporator would be a necessity if this system were to be used.

Much of the additional loading on components arises from the increased heat capacity at higher temperatures. It might well be that experimental values for the specific heats of solutions would be lower than the extimated values we have employed -- the effect, however, is expected to be real.

R-22 remains an interesting refrigerant candidate because of its availability, chemical stability and moderately high pressure which can favorably affect compactness of equipment.

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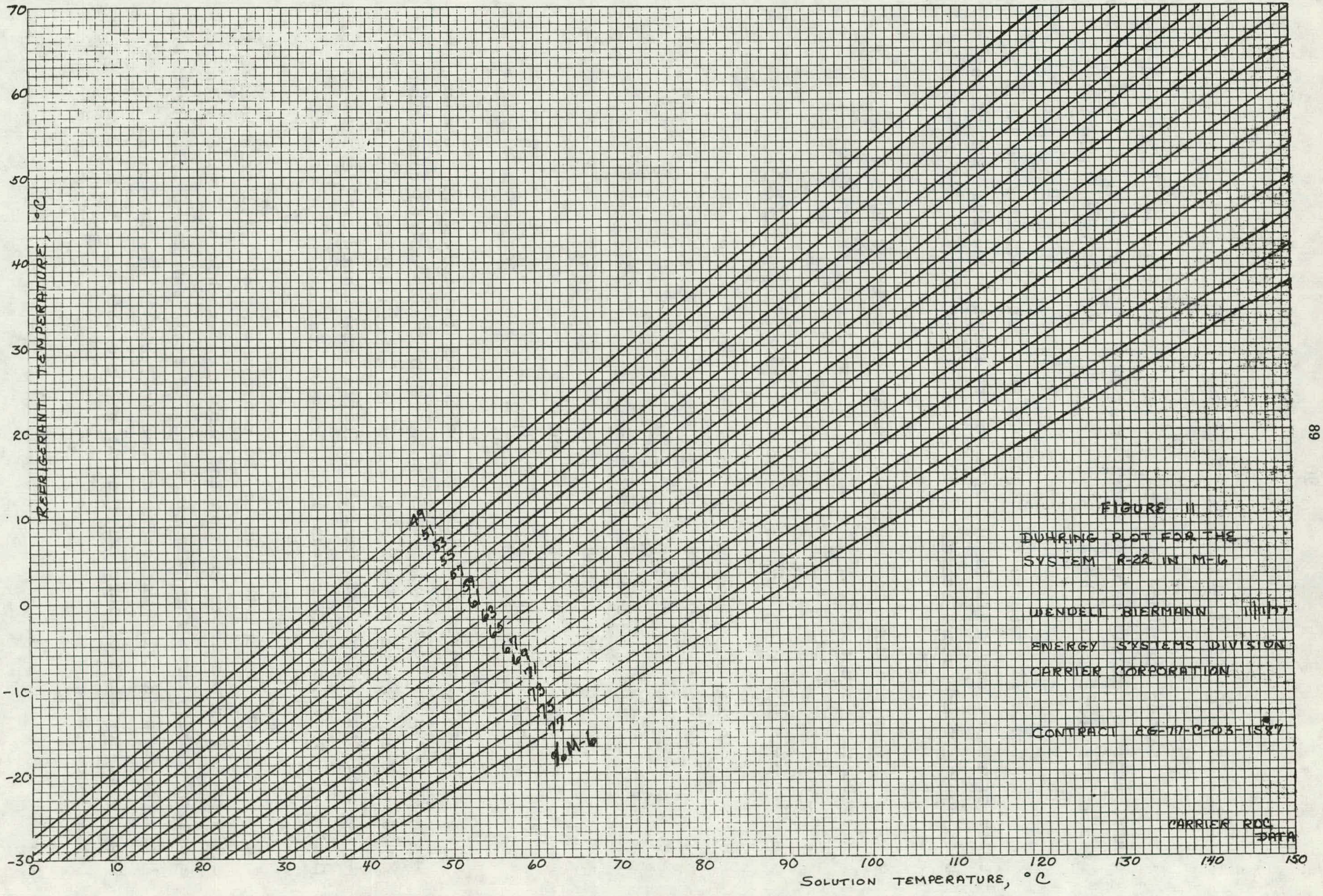

FIGURE 11

DUHRING PLOT FOR THE
SYSTEM R-22 IN M-6

WENDELL BIERMANN 11/11/77

ENERGY SYSTEMS DIVISION
CARRIER CORPORATION

CONTRACT EG-77-C-03-1587

4-1.7.1 Halogenated Ethane Refrigerants

Having concluded that the ethylene double bond is not an important contributor to bonding between refrigerant and absorbent, several halogenated ethanes were briefly explored.

Table 14 presents the vapor pressure data recorded for 1,1,2 trichloroethane and Table 15 shows vapor pressures of several solutions, both over a temperature range.

When the data in these two tables are combined into a series of linear Duhring equations, $T_{ref} = mT_{sol} + b$, we obtain the following:

Wt % M-12	m	b	T_{ref} (T_{sol} = 100°C)
16.13	0.9499	3.05	98.0
19.61	0.9168	-1.41	90.3
43.14	0.8581	-6.38	79.4
62.77	0.8507	-6.68	78.4
77.84	0.7684	-11.55	65.2
79.96	0.7908	-10.64	68.4
88.29	0.7402	-3.91	70.1

The column to the right is the calculated refrigerant temperature to be in pressure equilibrium with solution of the specified composition and 100°C. Since even at 90 wt % M-12 we cannot obtain a 50°C temperature difference, the approximate minimal criteria established earlier, we conclude that this system cannot be considered for air cooling.

In an attempt to enhance the poor showing of 1,1,2 trichloroethane, a fluorine atom was introduced on the number two carbon to further withdraw electron density from the hydrogen atoms. A small sample of 1,1,2 trichloro-2-fluoroethane (R-131a) was obtained and in Table 16 are presented the vapor pressure data of pure refrigerant and two solutions in M-6, over a temperature range.

TABLE 14

Vapor Pressure 1,1,2 Trichloroethane

T (°C)	P (in Hg)	T (°C)	P (in Hg)	T (°C)	P (in Hg)
20.2	0.60	60	4.82	85.0	12.35
25.0	1.00	65	5.93	87.5	13.45
30.0	1.31	70	7.20	90.0	14.70
35.0	1.64	72.5	8.01	92.5	15.95
40.0	2.00	75.0	8.78	95.0	17.30
45.0	2.58	77.5	9.51	97.5	18.61
50.0	3.15	80.0	10.35	100.0	20.10
55.0	3.90	82.5	11.35	102.5	21.65
				105.0	23.43
				107.5	25.24
				110.0	27.18
				112.0	29.00
				112.5	29.40

$$\ln P = \frac{m}{T} + b$$

$$= \frac{-4560.6}{T} + 16.463, \text{ P in kPa, T in °K}$$

TABLE 15

Vapor Pressures of 1,1,2 Trichloroethane in M-12

77.84% M-12		16.13 % M-12		79.96% M-12		43.14 % M-12	
T °C	P in Hg	T °C	P in Hg	T °C	P in Hg	T °C	P in Hg
25.0	0.40	20.0	0.70	25.0	0.30	20.0	0.40
30.0	0.50	25.0	1.05	30.0	0.50	25.0	0.55
35.0	0.55	30.0	1.39	35.0	0.60	30.0	0.67
40.0	0.65	35.0	1.71	40.0	0.75	35.0	0.87
45.0	0.80	40.0	2.03	45.0	0.95	40.0	1.10
50.0	1.00	45.0	2.59	50.0	1.14	45.0	1.37
55.0	1.25	50.0	3.20	55.0	1.43	50.0	1.71
60.0	1.55	55.0	3.98	60.0	1.78	55.0	2.08
65.0	1.85	60.0	4.81	65.0	2.10	60.0	2.52
70.0	2.20	65.0	5.90	70.0	2.55	65.0	3.12
75.0	2.65	70.0	7.08	75.0	3.10	70.0	3.78
80.0	3.12	75.0	8.46	80.0	3.70	75.0	4.52
85.0	3.70	80.0	10.15	85.0	4.42	80.0	5.40
90.0	4.40	82.5	11.11	90.0	5.18	85.0	6.45
95.0	5.11	85.0	12.02	95.0	6.09	90.0	7.57
100.0	5.91	87.5	13.16	100.0	7.03	95.0	8.99
106.0	7.50	90.0	14.30	105.0	8.12	100.0	10.38
110.0	8.10	95.0	16.60	110.0	9.32	105.0	12.00
115.0	9.17	97.5	17.82	112.5	10.08	107.5	13.05
120.0	10.50	100.0	19.16	115.0	10.80	110.0	13.85
125.0	11.80	102.5	20.72	117.5	11.60	112.5	14.80
130.0	13.40	105.0	22.25	120.0	12.32	115.0	15.81
		107.5	23.87	122.5	13.20	117.5	17.00
		110.0	25.40	125.0	14.08	120.0	18.37
		112.5	27.40	127.5	15.00	122.5	19.55
		115.0	29.45	130.0	15.84	125.0	20.84
		115.6	30.00	132.5	17.00	127.5	22.22
				135.0	17.83	130.0	23.62
				137.5	19.02	132.5	25.30
				140.0	20.02	135.0	26.97
				142.5	21.36	137.5	28.60
				145.0	22.60	139.5	29.95
				147.5	23.78		
				150.0	25.08		
				152.5	26.53		
				155.0	27.72		
				157.5	29.38		
				158.0	29.70		

TABLE 15 (cont'd.)

62.77 % M-12		88.29 % M-12		19.61 % M-12	
T °C	P (in Hg)	T °C	P (in Hg)	T °C	P (in Hg)
25.0	0.55	40.0	0.81	25.0	0.75
30.0	0.65	45.0	1.08	30.0	0.95
35.0	0.80	50.0	1.27	35.0	1.23
40.0	1.00	55.0	1.60	40.0	1.60
45.0	1.35	60.0	1.95	45.0	1.96
50.0	1.70	65.0	2.41	50.0	2.41
55.0	2.05	70.0	2.95	55.0	3.05
60.0	2.41	75.0	3.50	60.0	3.70
65.0	2.96	80.0	4.20	65.0	4.55
70.0	3.65	85.0	4.95	70.0	5.48
75.0	4.35	90.0	5.79	75.0	6.61
80.0	5.20	95.0	6.75	80.0	7.90
85.0	6.12	100.0	7.77	85.0	9.38
90.0	7.22	105.0	8.80	90.0	11.00
95.0	8.50	110.0	10.00	95.0	12.85
100.0	9.95	115.0	11.40	100.0	14.82
105.0	11.40	120.0	12.80	105.0	17.30
107.5	12.30	125.0	14.50	107.5	18.80
110.0	13.16	127.5	15.35	110.0	20.00
112.5	14.20	130.0	16.20	112.5	21.50
115.0	15.38	132.5	17.10	115.0	22.98
117.5	16.25	135.0	18.00	117.5	24.75
120.0	17.50	137.5	18.90	120.0	26.42
122.5	18.80	140.0	19.80	122.5	28.22
125.0	19.90	145.0	21.80	124.0	29.40
127.5	21.21	150.0	23.98	124.5	29.70
130.0	22.65	155.0	26.18		
132.5	24.07	160.0	28.40		
135.0	26.05	162.0	29.35		
137.5	27.30				

TABLE 15 (cont'd.)

77.84 % M-12		16.13 % M-12		79.96 % M-12		43.14 % M-12	
T °C	P in Hg	T °C	P in Hg	T °C	P in Hg	T °C	P in Hg
25.0	0.40	20.0	0.70	25.0	0.30	20.0	0.40
30.0	0.50	25.0	1.05	30.0	0.50	25.0	0.55
35.0	0.55	30.0	1.39	35.0	0.60	30.0	0.67
40.0	0.65	35.0	1.71	40.0	0.75	35.0	0.87
45.0	0.80	40.0	2.03	45.0	0.95	40.0	1.10
50.0	1.00	45.0	2.59	50.0	1.14	45.0	1.37
55.0	1.25	50.0	3.20	55.0	1.43	50.0	1.71
60.0	1.55	55.0	3.98	60.0	1.78	55.0	2.08
65.0	1.85	60.0	4.81	65.0	2.10	60.0	2.52
70.0	2.20	65.0	5.90	70.0	2.55	65.0	3.12
75.0	2.65	70.0	7.08	75.0	3.10	70.0	3.78
80.0	3.12	75.0	8.46	80.0	3.70	75.0	4.52
85.0	3.70	80.0	10.15	85.0	4.42	80.0	5.40
90.0	4.40	82.5	11.11	90.0	5.18	85.0	6.45
95.0	5.11	85.0	12.02	95.0	6.09	90.0	7.57
100.0	5.91	87.5	13.16	100.0	7.03	95.0	8.99
106.0	7.50	90.0	14.30	105.0	8.12	100.0	10.38
110.0	8.10	95.0	16.60	110.0	9.32	105.0	12.00
115.0	9.17	97.5	17.82	112.5	10.08	107.5	13.05
120.0	10.50	100.0	19.16	115.0	10.80	110.0	13.85
125.0	11.80	102.5	20.72	117.5	11.60	112.5	14.80
130.0	13.40	105.0	22.25	120.0	12.32	115.0	15.81
		107.5	23.87	122.5	13.20	117.5	17.00
		110.0	25.40	125.0	14.08	120.0	18.37
		112.5	27.40	127.5	15.00	122.5	19.55
		115.0	29.45	130.0	15.84	125.0	20.84
		115.6	30.00	132.5	17.00	127.5	22.22
				135.0	17.83	130.0	23.62
				137.5	19.02	132.5	25.30
				140.0	20.02	135.0	26.97
				142.5	21.36	137.5	28.60
				145.0	22.60	139.5	29.95
				147.5	23.78		
				150.0	25.08		
				152.5	26.53		
				155.0	27.72		
				157.5	29.38		
				158.0	29.70		

TABLE 16

VAPOR PRESSURE DATA 1,1,2 Trichloro-2-Fluoroethane (131a)

0.0 % M-6		83.43 % M-6		74.78 % M-6	
T °C	P cm Hg	T °C	P cm Hg	T °C	P cm Hg
26.5	9.90	24.6	0.40	39.7	1.00
28.5	10.70	56.0	1.80	57.6	2.30
30.0	12.22	81.4	4.50	68.8	3.90
33.2	13.25	87.2	5.70	77.6	5.30
36.3	14.90	93.0	7.25	87.0	7.90
39.4	17.40	108.2	11.95	99.1	12.00
41.7	18.65	113.5	13.80	112.0	18.10
44.6	19.90	122.8	18.65	117.1	21.80
46.6	22.55	130.1	23.80	122.7	25.30
53.9	28.70	135.7	27.15	127.9	29.25
55.3	30.9	143.9	32.80		
57.7	33.80	152.0	42.10		
59.6	36.00	161.4	52.65		
61.2	38.10	170.0	64.40		
63.1	40.50	175.1	72.50		
65.2	43.10				
66.8	45.65				
68.7	48.25				
72.7	54.30				
76.0	60.10				
79.2	67.45				
82.6	72.85				
84.0	75.20				

$$\ln P = \frac{m}{T} + b$$

$$= \frac{-3831.1}{T} + 15.374$$

(in kPa)

Combining these data into Duhring equations, we obtain:

Wt % M-6	m	b	T_{ref} (T_{sol} = 100°C)
83.43	0.7666	-52.57	24.1
74.78	0.8322	-52.01	31.2

The fourth column indicates that temperature differences between refrigerant and solutions in excess of our 50°C minimum can be obtained; other systems, however, show much more promise than this one.

What is demonstrated in this comparison of the two ethane derivatives is the effectiveness of a fluorine atom in promoting hydrogen bonding in these systems. This effect is generally seen in other comparisons which can be made with data contained in this report.

4-1.8.1 1,1,1-Trifluoro-2,2-dichloroethane (R-123b) and N,N-Dimethylhexamide (M-6)

Ths salutary effect of a fluorine atom, seen in the previous section, suggested that an even greater binding energy should result from the use of multiple fluorine atoms. As an experiment, a sample of 1,1,1-trifluoro-2,2-dichloroethane was obtained, its vapor pressure and vapor pressures of a series of solutions in M-6 measured and the Duhring equation constants shown below were obtained.

Table 16a. Duhring Constants, R-123b/M-6

Wt % M-6	m	b	T_{ref} (T_{sol} = 100°C)°C
91.96	0.5206	-63.2	-11.1
87.00	0.5544	-56.3	-0.9
81.42	0.6080	-54.3	6.5
79.68	0.6091	-50.2	10.7
73.26	0.6399	-47.3	16.7
69.58	0.6557	-43.2	22.4
68.74	0.6456	-38.3	26.4
63.68	0.6704	-37.2	29.8

$$T_{ref} = [0.8722 - 0.00348\,(x)]\,T_{sol} + 47.3 - 1.2283\,(x)$$

Figure 12 shows the loci of Duhring equations for integral values of the concentrations of M-6.

Looking at the refrigerant temperatures for 100°C solution temperatures, as shown in Table 16, we note that there has been little gain in going to the more highly fluorinated system, especially when the lower molecular weight of the M-6 is taken into account. Even more remarkable is the fact that if the generator and absorber concentrations are read off the curves (using 108°/47°C and 47°/6°C) they turn out to be substantially 59% M-6 in both cases.

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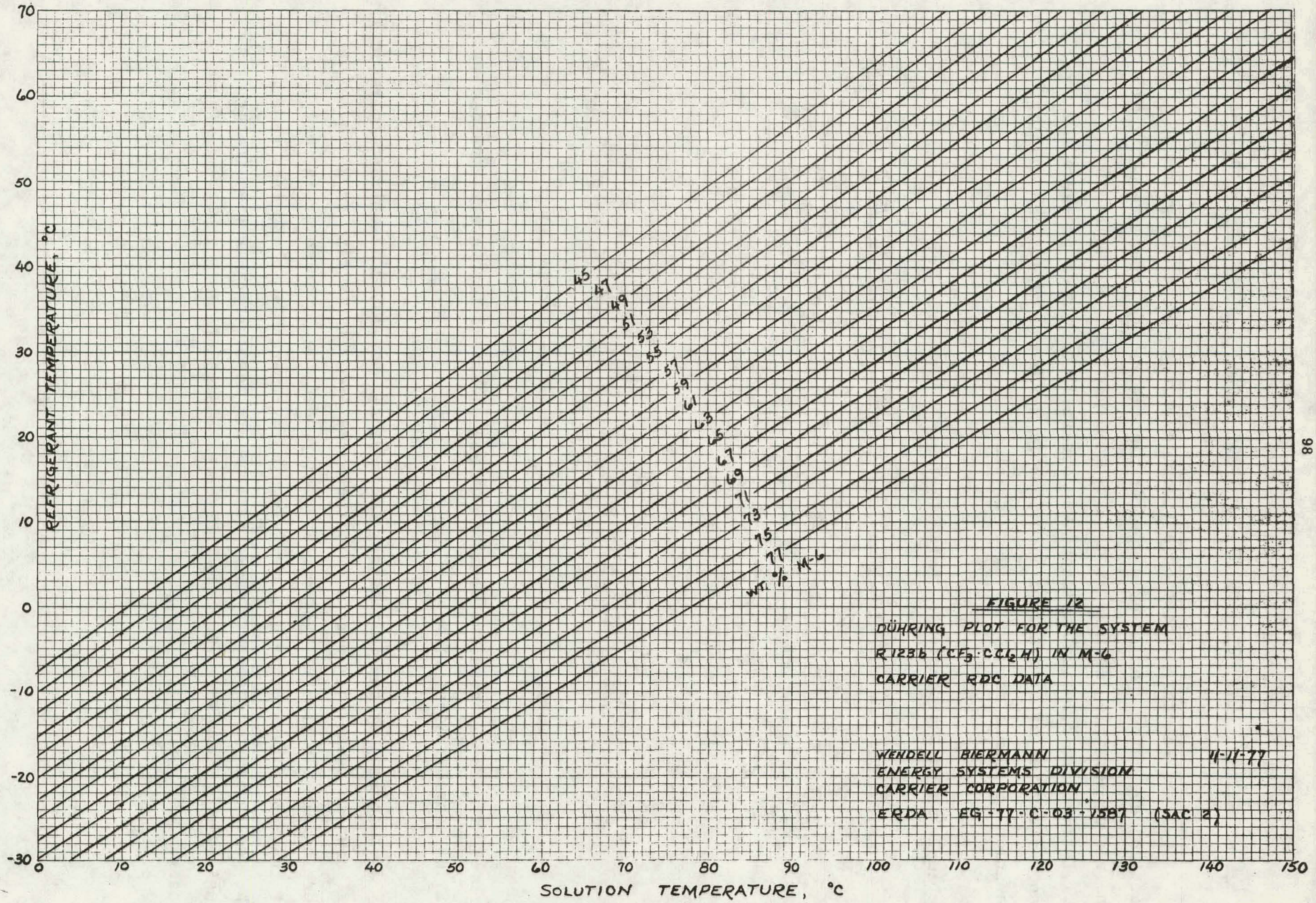

FIGURE 12

DÜHRING PLOT FOR THE SYSTEM
R 123b ($CF_3 \cdot CCl_2H$) IN M-6
CARRIER RDC DATA

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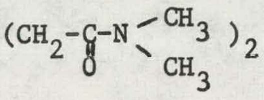
ENERGY SYSTEMS DIVISION
CARRIER CORPORATION
ERDA EG-77-C-03-1587 (SAC 2)

In all probability, the explanation of this lies in steric hindrance effects, the carbon atom on which the hydrogen bonding atom is located also contains three large substituent groups. This effect, good bonding but very small concentration change over the available temperature range, will be seen again, so it is probably a real effect and not just a poor set of data.

4-1.9.1 Multiple Dimethylamide Groups

Our basic postulate is that good absorption occurs because of hydrogen bonding to a specific site in the absorbent molecule, i.e., the carbonyl group in the dimethylamide structure. The remainder of the molecule serves only to polarize the bonding site and to add mass to decrease volatility. It appeared reasonable, therefore, to attempt to increase refrigerant solubility by replacing mere mass with a second functional group. Two such absorbents were prepared in the laboratory in sufficient amount to test the hypothesis; i.e.,

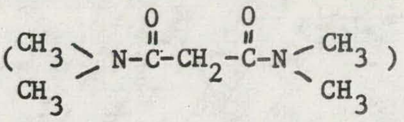
N,N,N',N'-tetramethylsuccinamide



$\left(CH_2-\underset{\underset{O}{\|}}{C}-N\begin{matrix}CH_3\\CH_3\end{matrix}\right)_2$

which is a solid melting at 84°C and

N,N,N',N'-tetramethylmalonamide



$\left(\begin{matrix}CH_3\\CH_3\end{matrix}N-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-N\begin{matrix}CH_3\\CH_3\end{matrix}\right)$

which is a liquid boiling above 250°C.

Vapor pressures of R-22 dissolved in each of these absorbents were measured over a range of concentration and temperature. The Duhring equation constants are tabulated in Table 17, and the loci of the equations at integral concentrations are shown in Figures 13 and 14.

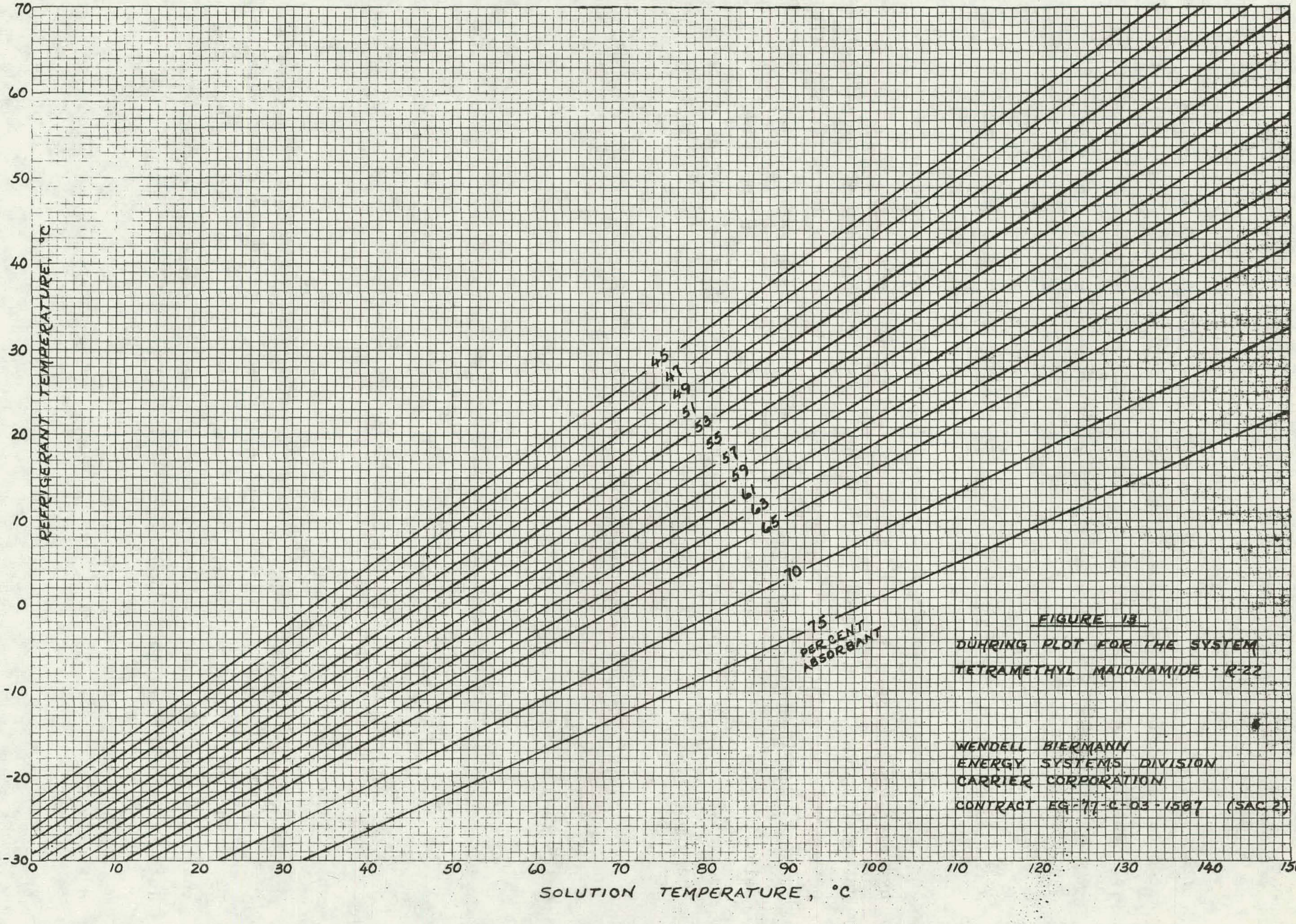


FIGURE 13

DÜHRING PLOT FOR THE SYSTEM TETRAMETHYL MALONAMIDE - R-22

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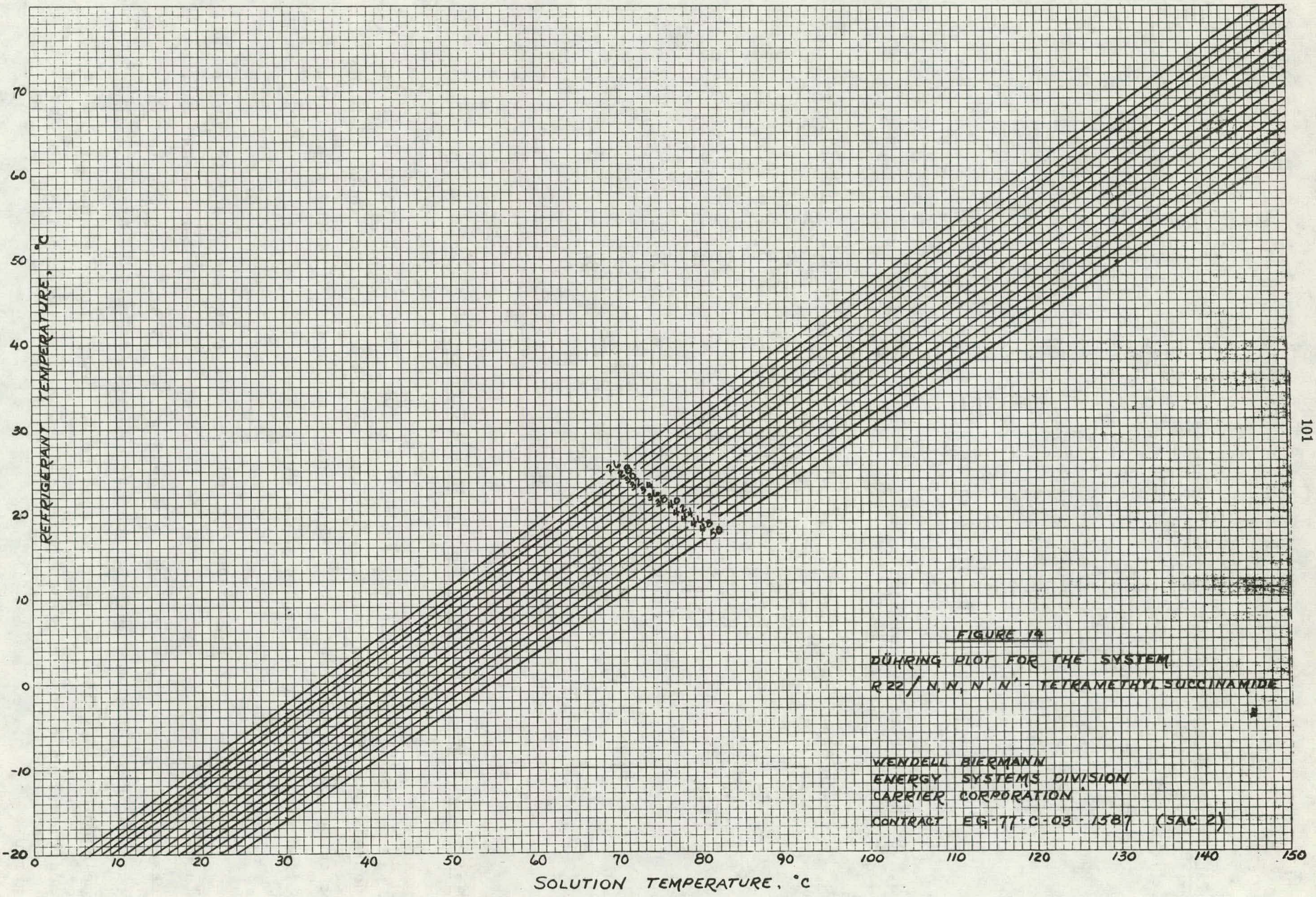

FIGURE 14

DÜHRING PLOT FOR THE SYSTEM

R 22 / N, N, N', N' - TETRAMETHYL SUCCINAMIDE

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Table 17. Duhring Equations R-22/Diamides

Wt % Abs.	m	b	T_{ref} (T_{sol} = 100°C)°C
54.0	0.6475	-40.2	24.6
45.5	0.6583	-29.1	36.7
29.3	0.7000	-26.5	43.5

$$T_{ref} = [0.7624 - 0.00218\ (x)]\ T_{sol} - 10.38 - 0.5017\ (x)$$

N,N,N',N' tetramethylmalonamide/R-22

Wt % Abs.	m	b	T_{ref} (T_{sol} = 100°C)°C
85.1	0.3773	-54.1	-16.4
74.1	0.4233	-39.9	2.4
65.5	0.5533	-37.1	18.2
55.6	0.5808	-29.2	28.9
48.8	0.6800	-28.7	39.3

$$T_{ref} = [1.068 - 0.00828\ (x)]\ T_{sol} + 7.47 - 0.6882\ (x)$$

4-1.9.2 Comments, Multiple Dimethylamide Groups

It is seen from Table 17 that both of these absorbents show large depressions of the dew point temperature at lower absorbent concentrations than we have seen previously. Thus, our basic approach of the advantages of multiple functional groups seems vindicated.

When we look for concentration spread between our standard conditions (generator 108°/47°C, absorber 47°/6°C) we see virtually zero spread in the case of the malonamide and only a modest 33.90% to 32.15% spread for the succinamide. This may well be another example of a steric effect -- the malonamide being less subject to the steric obstruction because of the additional unit in the carbon chain separating the two bonding carbonyl groups.

4-1.10.1 2-Pyrrolidone/R-22

Closely allied to the amides we have looked at are the pyrrolidones, such as 2-pyrrolidone $\underbrace{\mathrm{NH\text{-}CO\text{-}CH_2}}\mathrm{\text{-}CH_2\text{-}CH_2}$, which should be comparable in basicity to the amides, of slightly lower formula weight and commercially available in quantity. It has a melting point of 24.6°C and a boiling point of about 245°C. Like the amides, the pyrrolidones are excellent solvents for a wide variety of materials.

In Table 18 are collected the Duhring constants for the system R-22/2-pyrrolidone.

Table 18. R-22/2-pyrrolidone Duhring Constants

Wt % Abs.	m	b	$T_{ref}(T_{sol} = 100°C)$°C
92.88	0.6147	-68.59	-7.1
88.54	0.7508	-65.39	9.7
81.98	0.7750	-54.65	22.9
77.30	0.8224	-51.64	30.6
72.09	0.8228	-45.30	37.0
66.38	0.8155	-35.60	46.3

$$T_{ref} = [1.302 - 0.0067\ (x)]\ T_{sol} + 44.6 - 1.229\ (x)$$

Figure 15 shows the loci of these Duhring equations at integral values of concentration.

This is one of the more promising of the systems we have seen with a predicted 70.8 wt % concentration out of the generator and 64.6 wt % out of the absorber under our usual conditions of 108°/47°C generator and 47°/6°C absorber. This would work out to a weak solution circulation rate of 11.4 kg of solution per kg of refrigerant circulated.

No attempt is made to do a cycle calculation because it would be similar to the M-6/R-22 system already analyzed.

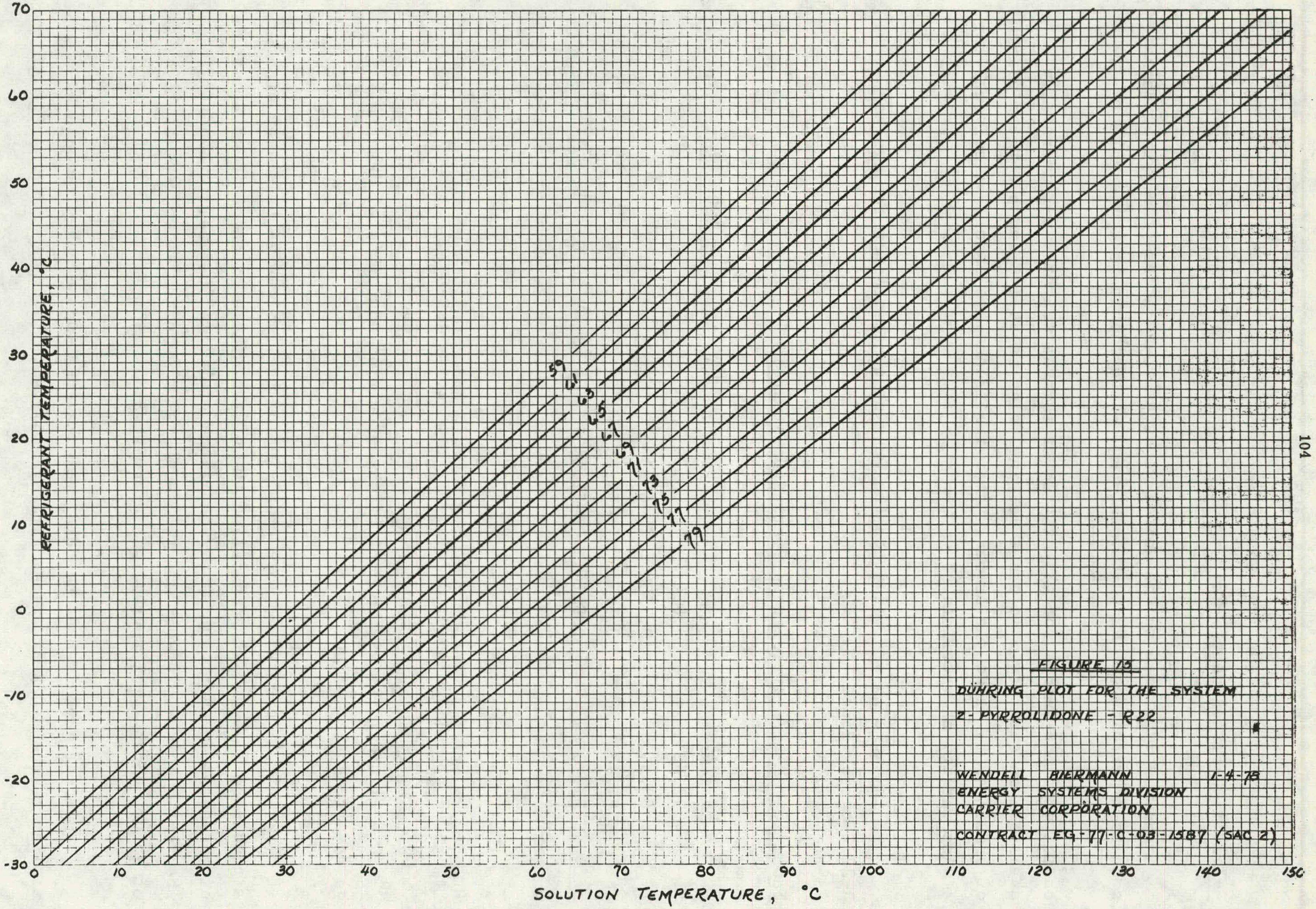

FIGURE 15

DÜHRING PLOT FOR THE SYSTEM

2-PYRROLIDONE - R22

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4-1.11.1 N-methyl-2-pyrrolidone Systems

Because of the promise of the 2-pyrrolidone/R-22 system, some data were collected with N-methyl-2-pyrrolidone $CH_3\text{-}\underbrace{N\text{-}CO\text{-}CH_2\text{-}CH_2\text{-}CH}_{}{}_2$ which should be somewhat more basic than 2-pyrrolidone and hence an improved absorbent. R-21, R-22 and R-123b ($CHF_2 \cdot C\,Cl_3$) were chosen as "better" refrigerants to pair with N-methyl-2-pyrrolidone.

Table 19 contains the Duhring constants obtained from the laboratory data for these three systems. The loci of these data, at integral concentrations, are shown in Figures 16, 17 and 18.

Concentrations and weak solution flow rates from these data are:

Refrigerant	(x) strong (108°/47°C)	(x) weak (47°/6°C)	w kg/kg ref.
R-21	55.1	53.6	36.73
R-22	50.8	45.0	8.76
R-123b	49.0	51.6	--

The expected improvement in solubility for R-22 is noted and reflected in a somewhat more reasonable circulation rate than we have generally seen. R-21 and R-123b are both larger molecules than R-22 and the less promising results for these can perhaps be related to steric effects.

TABLE 19. Duhring Constants for the Systems N-methyl-2-pyrrolidone/R-21, R-22 and R-123b

N-methyl-2-pyrrolidone/R-21

Wt % Abs.	m	b	T_{ref} (T_{sol} = 100°C)°C
80.0	0.6313	-55.77	7.4
76.0	0.6443	-51.05	13.4
72.0	0.6546	-46.30	19.2
68.0	0.6649	-41.75	24.7
64.0	0.6720	-37.28	29.9
60.0	0.6831	-33.61	34.7
56.0	0.7003	-30.20	39.8
54.0	0.7102	-28.37	42.7

$$T_{ref} = [0.8593 - 0.00286\ (x)]\ T_{sol} + 29.27 - 1.0534\ (x)$$

N-methyl-2-pyrrolidone/R-22

Wt % Abs.	m	b	T_{ref} (T_{sol} = 100°C)°C
88.10	0.4520	-65.98	-20.8
83.40	0.5085	-60.94	-10.1
74.30	0.6163	-56.51	5.1
67.51	0.6737	-50.67	16.7
60.10	0.7297	-45.30	27.7
52.08	0.7375	-36.38	37.4
49.52	0.7610	-34.21	41.9
48.15	0.7764	-32.76	44.9

$$T_{ref} = [1.157 - 0.00764\ (x)]\ T_{sol} + 5.22 - 0.8106\ (x).$$

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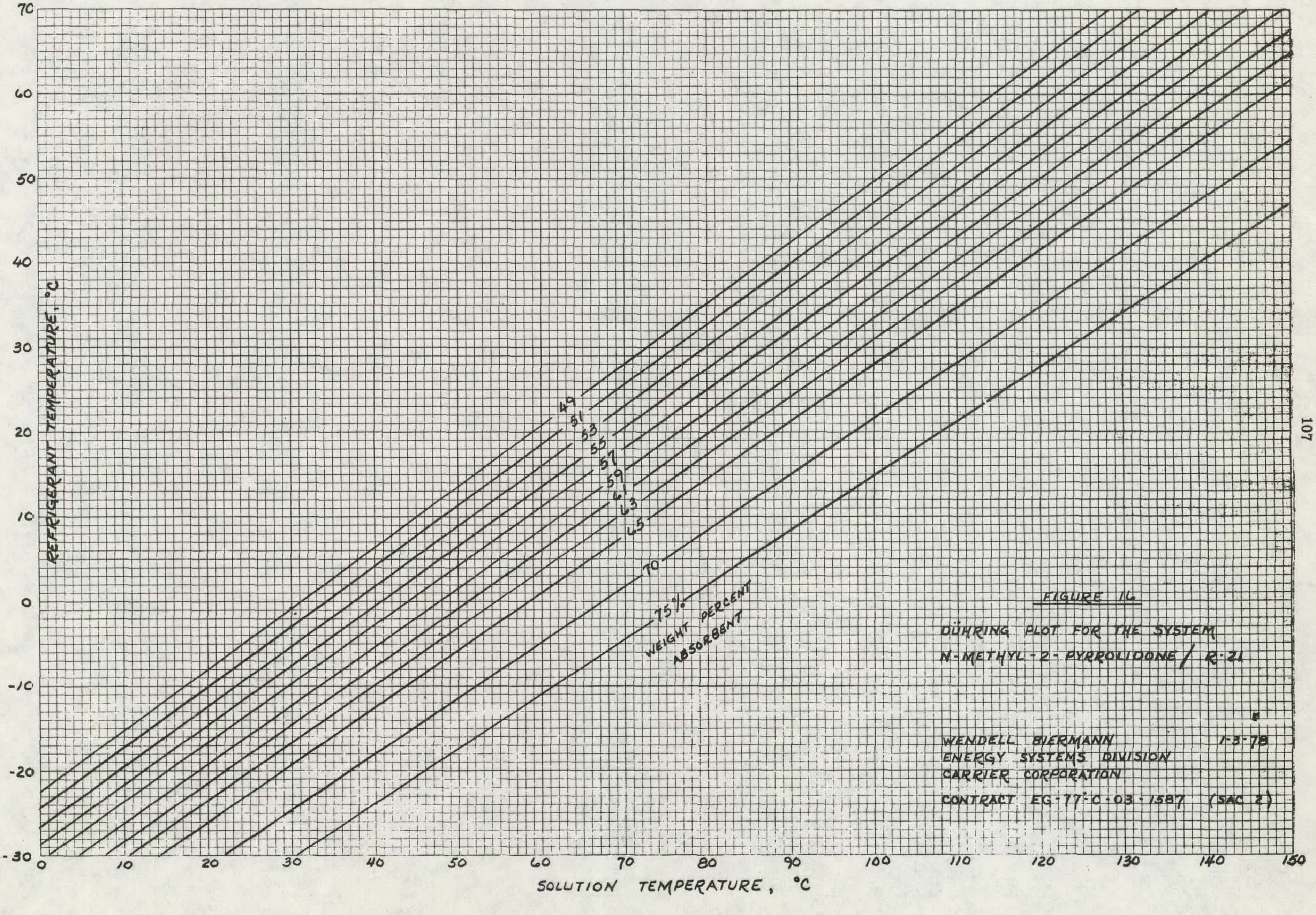

FIGURE 16

DÜHRING PLOT FOR THE SYSTEM
N-METHYL-2-PYRROLIDONE / R-21

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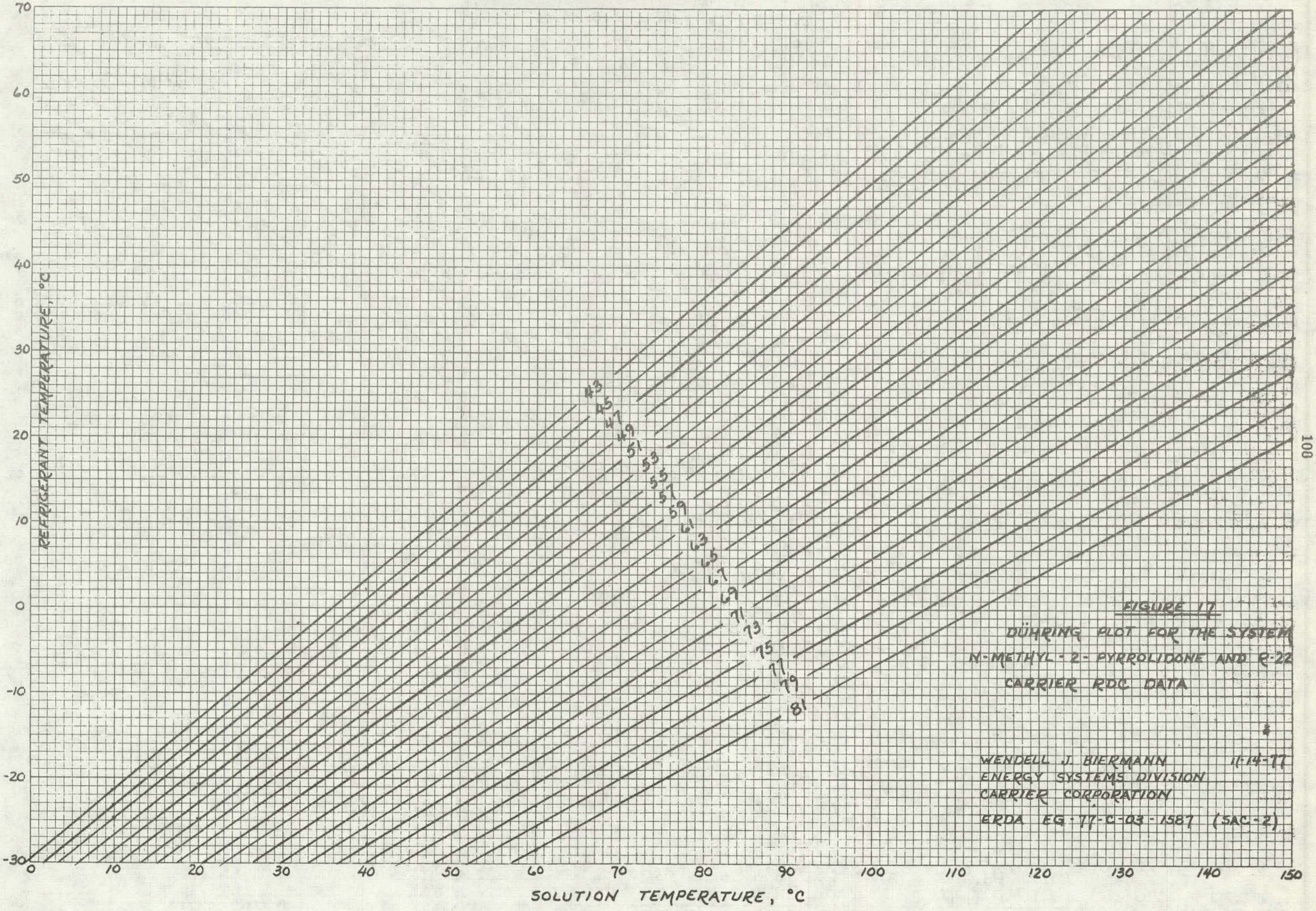

FIGURE 17

DÜHRING PLOT FOR THE SYSTEM N-METHYL-2-PYRROLIDONE AND R-22

CARRIER RDC DATA

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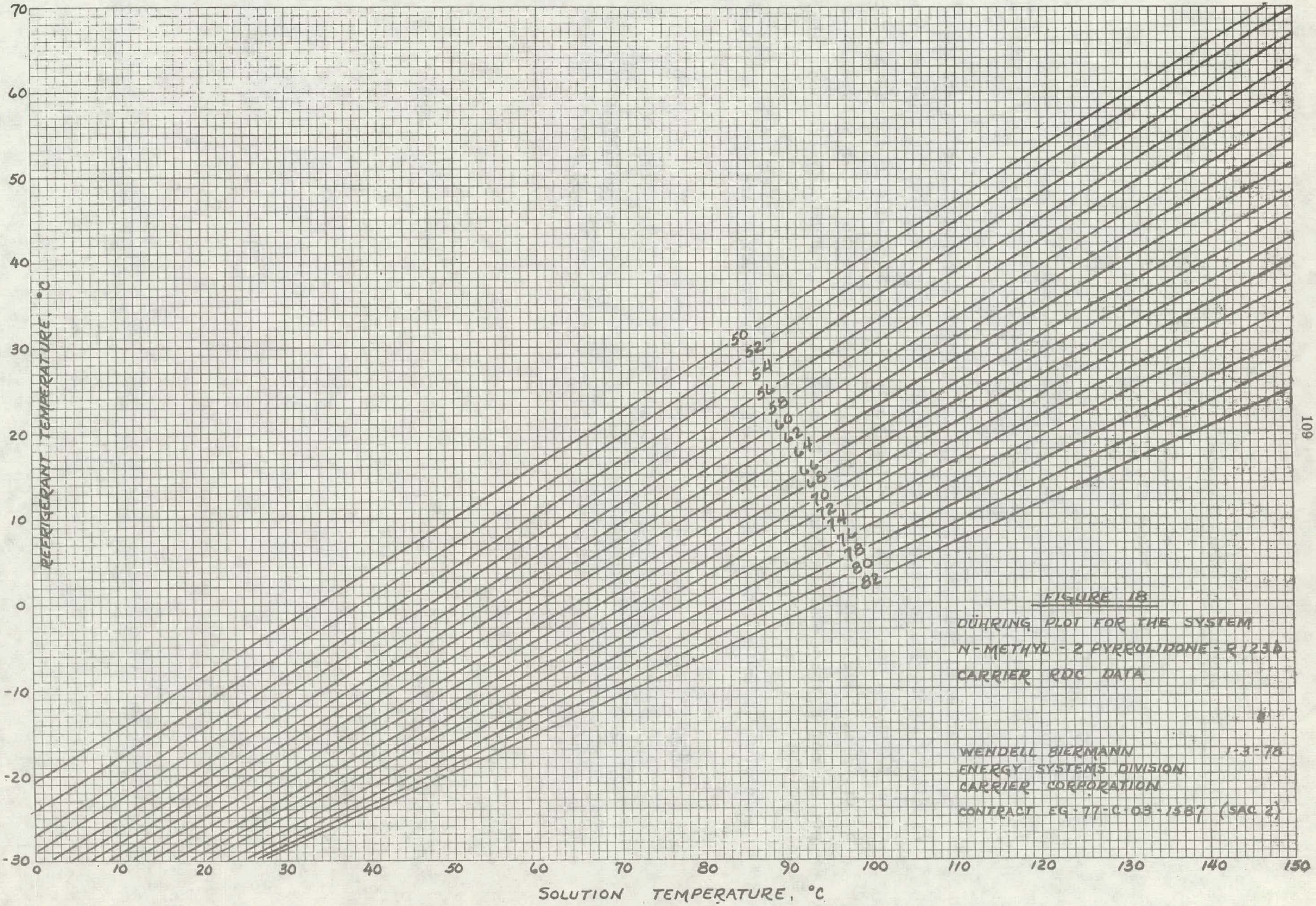

FIGURE 18

DÜHRING PLOT FOR THE SYSTEM
N-METHYL - 2 PYRROLIDONE - R123b
CARRIER RDC DATA

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CARRIER CORPORATION
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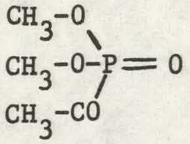
4-1.12.1 Trimethylphosphonoacetate/R-22

Trimethylphosphonoacetate,



$$\begin{array}{l} CH_3-O \\ CH_3-O-P=O \\ CH_3-CO \end{array}$$

is a liquid with a boiling point in excess of 250°C and is a good Lewis base.

Table 20 presents the Duhring constants for the three solutions studied. Appropriate interpolation leads to a strong solution concentration of 60.1% and a weak solution concentration of 62.5% which is the same sort of trend we have seen previously when the absorbent molecules become so pronouncedly three-dimensional as to make steric hindrances more possible.

Table 20. Trimethylphosphonoacetate/R-22 Duhring Constants

Wt % Abs.	m	b	T_{ref} (T_{sol} = 100°C) °C
78.6	0.6168	-49.0	12.7
66.8	0.7264	-36.5	36.1
57.8	0.8340	-28.0	55.8

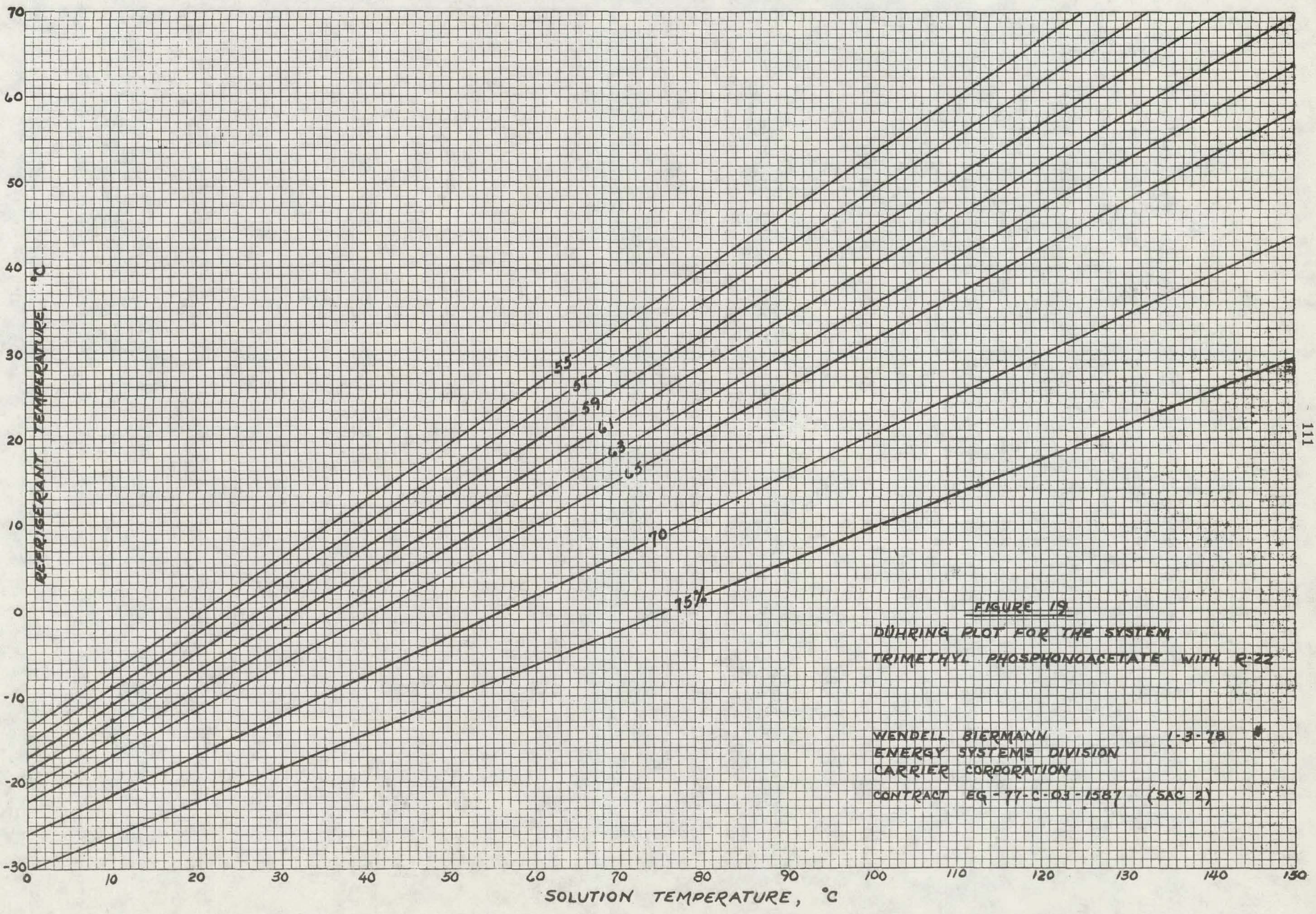


FIGURE 19

DÜHRING PLOT FOR THE SYSTEM
TRIMETHYL PHOSPHONOACETATE WITH R-22

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CARRIER CORPORATION

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4-2.1 Miscellaneous Systems

Table 21 presents single data points, at about ten weight percent refrigerant, for a number of systems closely related to those discussed in the body of this report. The last two columns to the right summarize the behavior. The ratio P/P (Raoult) gives the ratio of the experimentally observed pressure to that estimated from Raoult's Law, $P_R = N_{ref}P_{ref}$. It will be noticed that large refrigerant molecules with very weak interactions with absorbents lead to either very weak negative deviations, or even (as in case of CCl_4, $C_2H\ Br_3$ and R-113) large positive deviations. These are, of course, reflected in the right hand column which gives the temperature difference between the solution and the pure refrigerant when both show the vapor pressure of refrigerant at 30°C.

Table 22 presents a miscellany of mostly single point data which can be used to estimate degree of deviation from Raoult's Law, and hence, gain some indication of the Gibbs' free energy of solution.

TABLE 21

VAPOR PRESSURE DEPRESSION, MISCELLANEOUS SYSTEMS

System	Refrigerant $\ln P = A/T + B$		Weight % Absorbent	Mole Fraction Refrigerant	P/P (Raoult) (at 50°C)	$T_{sol} - T_{ref}$ (°C) ($T_{Ref} = 30°C$)
	A	B				
M-6/CH_2Cl_2	-3432.2	15.483	74.80	0.3618	0.56	48
M-6/CH_2Cl_2	-3432.2	15.483	89.19	0.1544	0.47	73
M-6/CCl_4	-3828.2	15.597	90.60	0.0868	1.17	63
M-6/Vinyl-acetonitrite	-4612.9	16.460	90.38	0.187	0.73	30.2
M-6/Properyl cyanide	-4479.5	16.296	91.90	0.1770	1.12	35.0
R-113/Tetraethylene glycol diethyl ether	-3492.7	15.513	91.26	0.0846	1.84	68
M-6/3-Chloropropene	-3569.1	15.855	90.65	0.1615	0.75	67.8
M-6/2,3-dichloropropene	-4194.7	16.136	91.53	0.1194	.72	63.1
M-6/2,3dichloro -1,1 difluoro 2-propene	-4701.1	17.819	90.27	0.0952	0.64	75.0
M-6/1,1,2 trichloro 3,3,3 trifluoropropene	-		90.90	0.0780	1.49	58.0
M-6/Tetrachloroethane	-4236.1	14.771	90.91	0.0785	1.79	48.0
M-6/1,1-difluoro dibromoethane			89.99	0.0599	0.82	74.2
M-6/Trans 1,4-dichloro 2-butene	-2712.2	10.515	90.62	0.1006	1.31	63
M-6/Tribromoethylene	-4734.2	15.550	90.63	0.0533	5.14	28.0

TABLE 22

HALOCARBON REFRIGERANTS PAIRED WITH VARIOUS ABSORBENTS

Refrigerant	Absorbent	Dew Pt. Lowering at 100°C Sol. Temp.	Refrig. Conc. Weight %
R-14 Carbon Tetrachloride	N,N-Dimethyl Amide M-6	66	9.5
R-20 Chloroform Trichloromethane	M-6	72.5	18
R-21 Dichlorofluoromethane	M-6	80	25
R-22	M-6	77.5	29
		100	18
		104.5	15.7
R-22	Vinyl-Pyrol	72.5	31
R-22	Sulfolane	70	23
R-22	Tributyl Phosphate	64	35.5
R-22	Propylene Carbonate	60.5	30.5
R-22	N,N-Dimethyl Formamide	104	22
R-22	Allyl Cyanide	80.5	25.5
R-23 Trifluoromethane	M-6	99	22
R-30 Dichloromethane	Sulfolane	25	40
R-30	M-6	47.5	25
R-32 Difluoromethane	M-6	54	31
Tetrachloroethane	M-6	53	9
1,1,2-Trichloroethane	M-12	29	17.5
Pentafluorochloroethane	M-6	111	8
Tetrachlorodifluoroethane	M-6	61	16
Dichlorotetrafluoroethane	M-6	40	26
Trichlorotrifluoroethane	Tetraethylene Pentamine	37	10

TABLE 22 (cont'd.)

HALOCARBON REFRIGERANTS PAIRED WITH VARIOUS ABSORBENTS

Refrigerant	Absorbent	Dew Pt. Lowering at 100°C Sol. Temp.	Refrig. Conc. Weight %
Trichlorotrifluoroethane	Tetraethylene Glycol Diethylether	70	9
Dichlorotrifluoroethane	Allyl Cyanide	56	29
Dichlorotrifluoroethane	M-6	77.5	30.5
		89	20.5
1,1,2-Trichloro-2-Fluoroethane	M-6	67.5	25
1,1,1-Trifluoro-2-Chloroethane	M-6	53	17
1-Chloro-1,1-Difluoroethane	M-6	59.5	18
1,1-Difluoro-1,2-Dibromoethane	M-6	73	10
Tetrachloroethylene	M-12	20	21
1,1-Dichloro-2,2-Difluoro ethylene	M-12	56	15.5
1,2-Dichloro-1,2-Difluoroethylene	M-6	55	22
Chlorotrifluoroethylene	M-6	75	16
Trichlorofluoroethylene	M-12	32	21
Bromotrifluoroethylene	M-6	79	15.5
1,2-Dichloro-1-Fluoroethylene	M-6	58.5	25
2-Chloro-1,1-Difluoroethylene	M-6	95	12
Tribromoethylene	M-6	32	9.5
Trichloroethylene	M-12	35	23
1-Chloro-2-Fluoroethylene	M-6	61.5	20
Cis-1,2-Dichloroethylene	M-6	72	14
Cis-1,2-Dichloroethylene	M-12	61	14.5
Trans-1,2-Dichloroethylene	M-12	58	15

TABLE 22 (cont'd.)

HALOCARBON REFRIGERANTS PAIRED WITH VARIOUS ABSORBENTS

Refrigerant	Absorbent	Dew Pt. Lowering at 100°C Sol. Temp.	Refrig. Conc. Weight %
1,2-Dibromoethylene	M-12	35	25.5
1,1-Dichloroethylene	M-12	65	13
Vinyl Bromide	M-6	80	9
2,3-Dibromopropene	M-6	46	9
2,3-Dichloropropene	M-6	64	8.5
3-Chloropropene	M-6	69	9
2,3-Dichloro-1,1-difluoro-2-propene	M-6	75	10
1,1,2-Trichloro-3,3,3-Trifluoropropene	M-6	61	9
Allyl Cyanide	M-6	40	10
Crotonitrile	M-6	45	9

5-0 FINAL COMMENTS

In terms of cycle performance, stability and availability, the most promising refrigerants for use with organic absorbents appear to be R-21 and R-22, each of which contains a single hydrogen atom for bonding with maximum enhancement of bonding tendency with the remainder of the refrigerant sites occupied by chlorine or fluorine atoms. R-21 may sometimes give steric problems because of the large size of two chlorine atoms; R-22 is a fairly high pressure refrigerant.

The predominate problem is the large amount of sensible heat which must be exchanged, this arising from two causes:

1. The low latent heat of vaporization of most refrigerants. The ratio of latent heat to specific heat constitutes a sort of "figure of merit" for refrigerants.
2. The small concentration difference permissible as a result of high absorber and low generator temperatures when solar energized, air cooled systems are considered.

In attempting to apply these systems (or most other systems, for that matter) one is faced with either constructing a solution heat exchanger with impractical, if not impossible, combinations of size, efficiency and pressure drop or else attempting to reduce the solution heat exchanger requirements by lowering the temperature differences between air and the interior of the absorber and condenser. This merely exchanges one difficult problem in heat transfer for another.

What accentuates the heat transfer problem is the rapid loss of coefficient of performance as even small percentages of sensible heat are lost rather than transferred. If cheap natural gas were to be the fuel (as was the object of most previous workers in this field), one could accept higher generator temperatures and lowered efficiency. Because of the high cost of amortizing an investment in solar collectors, neither of these two compromises is acceptable, since both involve using the collector array at reduced efficiency and hence higher cost per unit of useful energy. Even under the most favorable conditions the product of collector efficiency and chiller efficiency is going to be less than 50% on an instantaneous basis and perhaps half that over the operating portion of a day. Thus to produce 240 kWh of cooling per day ($\sim$3 tons for 24 hours) would require about

$$240 \div (0.25\ \text{kW/hr-m}^2 \times 10\ \text{h/day}) \cong 100\ \text{m}^2\ \text{collector}.$$

At present the cost of an installed collector is about $500/m^2 so that each percent loss in either collector performance or chiller performance is equivalent to something like $500 in capital cost or $50+ annual long term amortization cost. It is evident that very high efficiency cannot be compromised in a solar cooling system.

While one cannot categorically deny the possibility of constructing an air cooled, solar driven chiller, based on R-21 or R-22 and M-6 or 2-pyrrolidone, the problems are formidable and it appears to be the way of wisdom to seek among the higher latent heat refrigerants. For this reason, the subsequent review reports will cover only high latent heat refrigerants such as ammonia, methylamine and water which show considerably more promise.

In the experimental portion of this program, now in progress, the system selected uses water as refrigerant and internal heat transfer is similar in magnitude to equipment which has been commercially successful.

☆ G. P. O. 1978 – 740-306 / 9472, REGION NO. 4